NOAA Technical Memorandum OMPA-12

ORGANIC POLLUTANTS IN WATERWAYS ADJACENT

TO COMMENCEMENT BAY (PUGET SOUND)

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Boulder, Colorado November 1981



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Submitted to MESA Puget Sound Project Office of Marine Pollution Assessment

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SUMMARY

Hylebos and Blair Waterways, located adjacent to Commencement Bay in Puget Sound, are sites of high industrial activity. These waterways are dredged at regular intervals to permit ship traffic servicing the industry located adjacent to these waterways. Previous studies have shown sediment of these waterways to be contaminated with a variety of anthropogenic organic and inorganic toxicants.

In order to gain a better understanding of the current and historical input and distributions of anthropogenic organic toxicants, samples of water, suspended matter and sediment cores were collected from these two waterways in September and December 1980 for chemical analyses and for age dating.

Age dating of the sediment cores indicated the presence of recent (<25 year old) disturbed sediments and undisturbed sediments some of which appeared to be greater than 50 years old.

The highest concentrations of specific classes of organic pollutants resided in the more recent sediments. The major classes of organic pollutants identified were aromatic hydrocarbons ranging in molecular weight from naphthalene to perylene, chlorinated biphenyls containing from 1 to 6 chlorine atoms and chlorinated butadienes.

The highest concentrations of chlorinated biphenyls and chlorinated butadienes were found in sediments collected near the mouth of Hylebos Waterway. The source of the chlorinated biphenyls appears to be Arochlor 1242. The concentrations of a selected group of chlorinated biphenyls and chlorinated butadienes ranged from 383 to 7,272 $\mu g/kg$ and 2,127 to 77,098 $\mu g/kg$, respectively, in this area and were from 100 to 10,000 times higher concentrations than observed in other cores sampled from these two waterways. Age dating of the cores from this area suggests that accumulation of these components has been occurring over the past 20 years.

Aromatic hydrocarbons were found to be randomly distributed in the sediment cores with concentrations ranging from 216 to 104,889 $\mu g/kg$. High concentrations of naphthalenes were detected in surface sediments near the mouth of Blair Waterway. The source of these compounds appears to be the result of a recent spill or discharge of a petroleum distillate.

The concentrations and types of organic toxicants found in surface sediments examined in this study were in reasonable agreement with the chemistry of other sediments taken from the same area and analyzed by the National Marine Fisheries Service (Seattle, WA). However, this study shows that evaluation of the distributions and impact of organic toxicants at specific sites can be seriously underestimated if sampling is limited only to the examination of surface sediments.

All three classes of compounds found in the sediments (chlorinated biphenyls, chlorinated butadienes, aromatic hydrocarbons) were also found in suspended matter collected from both waterways with the chlorinated butadienes and chlorinated biphenyls also detected in the water, suggesting that these compounds are currently impacting the waterways.

In addition to these compounds, other volatile halogenated compounds (i.e., haloforms, 1,1,1-trichloroethane) were detected in water from these waterways. Their sources are most likely direct discharge or chemical formation as a result of discharge of active chlorine.

The surface microlayer sampled at locations in Hylebos and Blair Waterways did not contain detectable levels of soluble aromatic or halogenated organic compounds. Some samples, however, did contain detectable levels of 3-, 4-, and 5-ring aromatic hydrocarbons resulting from the presence of thin films of weathered oil present on the surface of the water. The source of these films of oil is most likely discharges from ships navigating the waterways.

Examination of the distributions of aromatic hydrocarbons and halogenated organic compounds between water, suspended matter and surface sediment indicated that significant amounts of chlorinated butadienes and the low molecular chlorinated biphenyls (Cl_1 through Cl_3) were present in the water column. The presence of the components in the water suggest that these compounds need further examination with respect to potential human health effects and impact to pelagic organisms.

Blair Waterway appears to be accumulating sediment from the Puyallup River. The turbid river plume is often observed near the entrance to Blair Waterway. This river plume appears to be diluting and/or minimizing the transport and deposition of the high concentrations of halogenated organics observed in water, suspended matter, and sediments near the mouth of Hylebos Waterway to the water column, suspended matter, and sediments of Blair Waterway and would suggest that the source of these chlorinated organic compounds be near the mouth of Hylebos Waterway.

Based on a sedimentation rate of 0.7 cm/year calculated from this study, fluxes of specific organic toxicants and classes of organic toxicants were determined. Total selected aromatic hydrocarbon input to Hylebos and Blair Waterways was estimated to be 13.7 and 14.5 kg/year, respectively. Input rates of benzanthracene and benz(e)pyrene were estimated to be 0.7 and 0.6 kg/yr for Hylebos Waterway and 0.4 and 0.2 kg/year for Blair Waterway. The estimated rate of input for the sum of two trichlorobutadiene isomers was 2.8 kg/year for Hylebos Waterway and 0.2 kg/year for Blair Waterway. The estimated rate of input of hexachlorobutadiene was 0.06 kg/yr for Hylebos Waterway and 0.01 kg/yr for Blair Waterway. The input of chlorinated biphenyls was estimated at 189 kg/year for Hylebos Waterway and 21 kg/year for Blair Waterway.

In summary, Hylebos and Blair Waterways are currently receiving input of anthropogenic organic toxicants and have received significant historical input of these same organic toxicants. Since these waterways have been dredged

every 6 to 10 years, transport of these contaminated sediments to relatively pristine areas of Puget Sound or use of the sediments in landfill could produce impacts for which the environmental consequences are unknown. Additional studies are needed to define the biological significance, if any, of these pollutants and to provide a data base necessary for formulating rational decisions on the future management of waterways impacted by toxic organic substances.

1. INTRODUCTION

Recent research studies whose objectives have been to investigate the organic chemical composition of sediments, suspended matter and water of estuarine and freshwater environments have provided an increasing awareness of the sources, distributions and transport of toxic organic substances entering water bodies as a result of man's activities (Hites and Biemann, 1972; Helz and Hsu, 1978; Sheldon and Hites, 1978; Windsor and Hites, 1979; Sheldon and Hites, 1979; Lake et al., 1979; Prahl and Carpenter, 1979; Pavlou and Dexter, 1979; Nelson and Hites, 1980; Hites et al., 1980; Bopp et al., 1981; Lake et al., 1981). Many of these substances have been designated by the U.S. Environmental Protection Agency as priority pollutants (Ambient Water Quality Criteria, 1979) and are currently under experimental study with respect to their effects on water quality, fates in the environment and potential food chain transport.

The MESA Puget Sound Project was established within the Marine Ecosystems Analysis Program (MESA), a part of the National Oceanic and Atmospheric Administration (NOAA), to focus scientific research on specific environmental problems relating to Puget Sound, some of which relate to the insult of specific toxic organic substances as described above. The specific goals of the project were to: 1) assess critical environmental problems in Puget Sound waters, 2) determine the effects of critical environmental stress within the Puget Sound ecological systems, and 3) identify and characterize the major marine components and processes of Puget Sound ecosystems which are involved in critical environmental problems.

There are several littoral regions of Puget Sound that are highly industrialized and it is anticipated that expansion of the industrial base will continue. The organic chemical composition of water and suspended matter collected from several locations in Puget Sound was recently investigated to determine occurrence, if any, of selected potentially toxic organic compounds and metals (Riley et al., 1980). The results of these studies indicated that while the water column (water-suspended matter) from most sampling sites studied appeared to be relatively uncontaminated, halogenated organic compounds were detected in the water and suspended matter of two waterways (Hylebos and Blair) located adjacent to Commencement Bay, Washington (Figs. 1 and 2).

Sediments from the waterways have been shown to contain halogenated organics (chlorinated olefins, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and elevated concentrations of certain metals (arsenic and lead). In addition, demersal and benthic organisms were shown to accumulate

some of these same components (Malins et al., 1980). The same study has examined the relationship between the presence of these contaminants and increased frequencies of tumors and lesions in fish and invertebrate species residing in this area. However, the study indicates a need for further research to establish possible cause and effect relationships.

Previously reported chemical analyses of sediments collected from Hylebos and Blair Waterways have focused mainly on the chemical composition near the sediment surface (Malins et al., 1980). In addition, little published information is available regarding the chemical composition of suspended matter and water from these same waterways (Riley et al., 1980). Because of the limited information available on the chemistry of these ecological compartments, our understanding of recent and historical input of natural and anthropogenic pollutants to these waterways is limited.

Despite the absence of this type of information, Hylebos and Blair Water-ways have previously been dredged on six to ten year cycles and the dredged spoils disposed of in other areas of Commencement Bay and on the adjacent shore. Thus, the past and future impact to other areas of Commencement Bay as a result of such a disposal practice is unknown.

This report discusses the results of a study sponsored by the MESA Puget Sound Project to 1) examine the distributions of selected toxic organic compounds in water, suspended matter and sediment collected from selected locations in Hylebos and Blair Waterways, 2) gain a better understanding of the historical accumulation of selected toxic organic substances through analyses of stratified, age-dated sediment cores, and 3) gain a better understanding of the current fluxes of these selected toxic organic substances to these waterways.

Results of the investigation have been used to gain a better understanding of recent and historical input and the distributions of organic pollutants to these waterways. Such knowledge is necessary for formulating rational decisions on the future management of waterways impacted by toxic organic compounds.

2. METHODS AND MATERIALS

2.1 Sampling Areas and Sampling Sites

Figure 3 shows the location of the 10 specific sites for the collection of water, suspended matter and sediments during sampling cruises to Hylebos and Blair Waterways in September and December of 1980.

2.2 General Sampling Strategy

Sampling was conducted from an anchored research vessel. Water and suspended matter samples were collected during both sampling cruises; however,

sediment cores were collected only during the September cruise. The sediment coring stations were selected with the intention of collecting undisturbed sediment that would have accumulated during the last several decades and therefore hold a record of the organic chemical pollution in the two waterways of Commencement Bay. Because sections of the waterways are dredged periodically to maintain a navigation channel, the sedimentary record both in the waterway channels and nearby areas may have been disturbed. The cores were generally collected near the edge of the dredge channel in the vicinity of suspected toxic chemical sources such as chemical plants. Several coring attempts were made on steeply sloping sides of the waterway instead of from the relatively flat channel but the sides were compact deposits of clay and could not be In the central region of Hylebos Waterway (Station 4) a shallow subtidal area located near the dredged channel was cored. This core consisted of sandy sediments and is not a recent sediment accumulation site as demonstrated by the low levels of $^{137}\mathrm{Cs}$ and $^{210}\mathrm{Pb}$ in these sediments. From our coring experience it appears that sediments are accumulating only on the bottom of the dredge channels and not on the steep sides of the channels, nor in the few sandy flats adjacent to the channels. During the coring operation the divers noticed the length of the cores in the core barrels were often shorter than the depth to which the barrel penetrated the bottom. This shortening effect, which frequently occurs with gravity cores, is the result of both compressing the sediment column and also pushing sediments away from the core barrel openings as the barrel fills with sediments. Instead of the barrel passing down through the sediment, the partly-filled barrel acts as a solid object, merely displacing the sediment; not coring. Once the core barrel had penetrated the sediment to 50-cm depth, the divers dug down and capped both ends of the barrel before removing the core.

Samples of suspended matter and filtered water sampled by way of the XAD-2 resin method were collected at two sites as a function of 3 water depths in the vicinity of suspected toxic chemical sources. The site in Hylebos Waterway (Station 5) was located slightly up the waterway (see Figure 3) from the site used for the collection of water and suspended matter the previous year (Riley et al., 1980); whereas water and suspended matter from Blair Waterway were collected from the same site (Station 8) used the previous year for collection of similar samples. Thus, some comparisons between data collected from the previous year's study to this year's data are possible. Sampling of suspended matter and water from both sites during each cruise occurred on both in-coming and out-going tides, thus permitting an opportunity to further examine the possible influence of suspected toxic chemical sources on chemical composition of water and suspended matter from these areas.

Water samples for analysis of volatile organic compounds employing the "purge and trap" method were collected from several sites located in both waterways. In Hylebos Waterway, samples were collected below, adjacent to and above two suspect areas of chemical discharge (near Stations 3, 5, and 6). In Blair Waterway, samples were taken below, adjacent to and above a known bank seep situated below Station 9. Sampling of these areas also permits comparison of our data with similar data generated by other agencies (e.g., Environmental Protection Agency) who have previously conducted similar surveys of Hylebos

and Blair Waterways. Samples ("purge and trap") collected near Stations 5, 6, 8 and 9 were collected during the December cruise. Samples near Station 3 were collected during the September cruise.

Sampling of the surface microlayer occurred at Stations 5 and 8 and were examined for enrichment in organic compounds. Samples of phytoplankton were collected for microscopic examination and an analysis for organic pollutants. However, after examination it was determined that insufficient material was available for extraction and chemical analysis although the microscopic examination was conducted and is reported on in this document.

Sediment cores were collected in Hylebos and Blair Waterways by SCUBA divers. Suspended matter was collected for organic chemical analysis by pumping seawater through glass filters. Simultaneously, dissolved hydrophilic organic compounds were concentrated by pumping the glass filtered seawater through stainless steel columns packed with XAD-2 resin. Samples of water for analysis of volatile hydrocarbons by the "purge and trap" method were collected by sealing, with septum caps, glass bottles that were completely filled with seawater. Surface microlayer samples were collected by dipping a clean sheet of glass vertically in and out through the surface. Phytoplankton samples were collected by sequential filtrations of water through a 243 μm and then 64 μm plankton net which retained the phytoplankton. Conventional methods were used for sampling and analysis of chlorophyll, particulate organic carbon, dissolved organic carbon, salinity, dissolved oxygen and particle size distribution (see Appendix A for details of sampling methods).

2.3 General Analytical Strategy

A brief summary of the analytical methods is presented here (see Appendix B for details of analytical methods). Volatile organics were sparged from seawater with a stream of nitrogen gas and adsorbed on a $\mathsf{Tenax}^{\mathsf{B}}$ Column ("purge and trap" method). Characterizations and quantifications of these compounds were determined by their release from the Tenax resin into a gas chromatographic column mounted in a gas chromatograph/mass spectrometer (GC/MS). Dissolved lipophilic organic compounds that had been preconcentrated on columns containing XAD-2 resin were eluted with ethyl ether. The concentrated ethyl ether extracts were qualitatively and quantitatively analyzed by capillary gas chromatography for halogenated organics. Samples of the surface microlayer were extracted with organic solvents. The concentrated solvent extracts were concentrated and fractionated by silica gel chromatography. The aromatic fraction, which contains both aromatic hydrocarbons and lipophilic halogenated organic compounds, was concentrated and subjected to capillary gas chromato-Suspended matter was Soxhlet extracted with benzene/ graphic analysis. The concentrated aromatic hydrocarbon fraction was prepared for GC analysis as described above for surface microlayer samples. Sediment samples were first dewatered by shaking with methanol and then Soxhlet extracted and prepared for GC analysis as described for suspended matter and surface microlayer samples. 137_{Cs}. Samples Samples of sediment were age-dated by counting of ²¹⁰Pb and Samples of sediment from the cores were dried, pressed into pellets and subjected to gamma counting. Samples of phytoplankton were examined microscopically. The overall sampling and analytical scheme is shown in Fig. 4. There are literally hundreds of individual aromatic hydrocarbon and PCB toxicants associated with environmental samples. However, only a limited number of these compounds are available as analytical standards. For the purpose of this study we limited our analyses of water, suspended matter, and surface microlayer to a select group consisting of 18 aromatic hydrocarbons (naphthalene to perylene in molecular weight range), 5 individual chlorinated biphenyls (Cl₁ to Cl₅), and 3 chlorinated butadienes. Using these 26 compounds, we could examine the relative concentrations of these classes of compounds in the various environmental compartments.

3. RESULTS

3.1 General Physical and Chemical Parameters

The physical and chemical parameters measured in September and December are typical values for the time of the year (Tables 1 and 2) and agree with those reported for September and November of 1979 (Riley et al., 1980). Salinity increased with depth during both September and December indicating a halocline was present probably caused by the plume of the Puyallup River. Temperature decreased with depth in September but was uniform in December.

Suspended load ranged from 2 to 9 mg/l and was generally higher in the near-bottom samples. DOC ranged from approximately 1 to 2 mg C/l and POC 0.1 to 0.3 mg C/l. Percent organic carbon of the suspended matter ranged from 2 to 12%. Chlorophyll was 5 times higher in September than December and is probably due to higher phytoplankton standing stock when the water column was more strongly stratified and light more intense.

3.2 Volatile Hydrocarbons in Water

3.2.1 Purge and Trap Analysis

The results of our analysis of waters from Hylebos and Blair Waterways for volatile organic compounds using the method of "purge and trap" are shown in Table 3. Chemical analysis of a systems blank showed peak response at retention times for methylene chloride, 1,2-dichloropropane, dichlorobromomethane, 1,1,1-trichloroethane, benzene and toluene. The interpretation of the "purge and trap" data that follows takes into account these background levels. Total concentrations of volatile hydrocarbons detected in waters collected from Station 5 and adjacent sites near suspect areas of chemical discharge in Hylebos Waterway and Station 8 and sites near a bank seep in Blair Waterway in December ranged from 22.9 ppb to 53.9 ppb. The major contributor to the total volatile hydrocarbons detected in waters collected at Station 5, Station 8, areas below and adjacent to the bank seep and above a point of suspect

discharge near Station 5 was 1, 1, 1-trichlorethane. The percent total volatile hydrocarbon contribution of this component ranged from 76.3 to 91.9%. Water sampled above the discharge point of the bank seep as well as at sites sampled below and adjacent to a point of chemical discharge near Station 5 contained significant levels of toluene. The range in percent contribution of 1, 1-trichloroethane to total concentration of volatile hydrocarbons detected in these samples was 56.3 to 69.8%. The range in the percent contribution of toluene was 22.9 to 30.8%.

In contrast, samples of water collected at sites located below, adjacent to and above a suspect point of chemical discharge near Station 3 in September contained lower total concentrations of volatile hydrocarbons (11.6-14.3 ppb) than water samples collected on the December cruise. This difference in total volatile hydrocarbons is, for the most part, totally accounted for in the absence of significant concentrations of 1, 1, 1-trichloroethane in these waters in September.

Bromoform was detected in quantifiable levels in waters surrounding suspect discharges near Stations 6 and 3 and at Station 5 but not at Station 8 or in waters surrounding the bank seep. Chloroform was present in all water samples but at 5 to 7 times higher levels in waters at Station 5 and water surrounding suspect discharge points near Stations 6 and 3 as compared to waters analyzed from Station 8 and water surrounding the bank seep. Similar results were found for the compound, trichloroethylene. Methylene chloride and benzene appeared to be present in all samples. However, because of high background levels and sample variability, it is difficult to assess the distribution of these compounds among the samples analyzed. It would appear that the distribution of tetrachloroethylene followed that of trichloroethylene, with concentrations somewhat lower. In some instances, the compounds 1,2-dichloroethylene, dibromochloromethane, 1,2-dichloropropane and dibromochloromethane were detected but were considerably below the threshold levels necessary to accurately assess their distributions.

3.2.2 Volatile Halogenated Hydrocarbons in Filtered Water (Qualitative)

Concentrated solvent extracts containing organic compounds obtained by sampling water at all stations from both sample cruises by the XAD-2 resin method were directly examined by capillary gas chromatographic analysis employing an electron capture detector. Lower retention time components were observed eluting from the column some of which most likely corresponded to volatile halogenated compounds previously described and analyzed by the "purge and trap" method. Samples analyzed from Stations 4, 5 and 6 produced the greatest response to electron capturing components in this region and the PCB region of the chromatograms relative to all other sampling stations from both sampling cruises. An electron capturing component which matched in retention time to that of hexachlorobutadiene (HCBD) was detected and found to be in higher concentrations in all XAD-2 water samples analyzed from both sampling cruises from Hylebos waterway as compared to concentrations determined in water samples collected from Blair waterway. A similar trend appeared to exist for two trichlorobutadiene isomers. In Fig. 5 representative gas chromatograms

show electron capturing components in filtered water collected from Stations 5 and 8. Since none of the common pesticides and pesticide by-products (lindane, dieldrin, heptachlor, aldrin, p,p'-DDD, p,p'-DDT, p,p'-DDE, endrin, methoxy-chlor or chlorinated benzenes) were detected by single-ion GC/MS in samples of suspended matter or sediment containing the highest level of electron-capturing activity, these components could not be quantified in samples of filtered water. GC/MS analysis could not be conducted on filtered water samples (concentrations of individual components were below the limit of detection); thus, the basis for quantification for halogenated organics in water was retention time congruency to those same compounds identified in suspended matter and sediment by GC/MS.

3.2.3 Volatile Halogenated Hydrocarbons in Filtered Water (Quantitative)

Detectable concentrations of hexachlorobutadiene in filtered water ranged from 1 to 18 parts per trillion (pptr) with the highest concentrations appearing in water samples collected from Stations 1-7 (Table 4). Detectable concentrations of two trichlorobutadiene isomers ranged from 3 to 252 pptr. concentrations of these components appeared in surface waters compared to deeper waters at Station 5 with the reverse occurring at Station 8. In contrast, detectable concentrations of a selected group of individual chlorinated biphenyls ranged from 1 to 317 pptr with the mono- and dichlorinated biphenyls being present in the highest concentrations. These concentration distributions would be expected based on their slightly higher water solubility. concentrations of total selected chlorinated butadienes and chlorinated biphenyls appeared in waters collected from Stations 5 and 6. As with the chlorinated biphenyls, the highest concentrations of chlorinated butadienes were observed to be associated with the two "trichloro" isomers. Concentration levels for all components measured did not appear to differ significantly when comparing samples collected from the different cruises. In addition, no clear pattern emerged to indicate a correlation of concentration of these individual components with depth with the possible exception of the trichlorobutadiene isomers (Table 4). Series-coupled columns were pumped at Station 8 in December and analyzed individually to obtain information regarding the efficiency of retention of the individual halogenated organic compounds listed in Table 4. Retention of hexachlorobutadiene appeared to be about 69% on the top column indicating the concentrations reported for this component in Table 4 to be low by a factor of 2 (see footnote 3 in Table 4 for method of calculation). trichlorobutadiene isomers appeared to vary considerably in their adsorption to XAD-2 resin. Trichlorobutadiene-2 was efficiently retained whereas retention of the other isomer (trichlorobutadiene-1) ranged from 19 to 48%. The efficiency of retention of the monochlorobiphenyl ranged from 40 to 65% with the dichlorinated biphenyl more efficiently retained at 69 to 83%. The range in the amount retained of the trichlorinated biphenyl was 51 to 85%. We were not able to determine the efficiency of retention of Cl₄ and Cl₅ biphenyls because of the very low levels and, in most cases, absence of detectable levels of these components. These results indicate that concentrations reported in Table 4 for the mono-, di-, and trichlorinated biphenyls are low but in the most inefficient case (monochlorobiphenyl) not lower than about a factor of two. In general, values reported in Table 4 are conservative estimates of the absolute concentrations of these components in the water column.

3.3 Analysis of Surface Microlayer

3.3.1 <u>Aromatic Hydrocarbons</u>

Surface microlayer samples collected from Stations 5 and 8 during both sampling cruises were analyzed by capillary gas chromatography for the presence of halogenated and other volatile aromatic hydrocarbons. No halogenated components were detected by electron capture gas chromatography in any of the surface microlayer samples collected during both sampling cruises. Table 5 lists the results of our analyses of these samples for a select group of volatile aromatic hydrocarbons. Figure 6 shows capillary gas chromatograms of the aromatic fractions isolated from the surface microlayer from Stations 5 and 8 during the September and December sampling cruises. Samples collected from Station 5 during the September sampling cruise did not contain detectable levels of volatile hydrocarbons (<5.0 ppb, <4.6 ppb; Table 5). However, samples collected in December from the same station contained detectable levels of 3-, 4-, and 5-ring aromatic hydrocarbons. Total concentration of aromatic hydrocarbons for the duplicate analyses were 62.3 + 8.6 ppb. Major components present included phenanthrene, fluoranthene, pyrene, benzanthracene and chry-Samples collected from Station 8 during both sampling cruises contained detectable levels of the same aromatic hydrocarbons (19.7 ppb, 164.4 + 71.4 However, unlike the 12/80 and 9/80 samples analyzed from Station 5 and 8, respectively, the gas chromatographic patterns of water samples analyzed from the Station 8 (12/80) sampling appeared to have the characteristics of a highly weathered oil. The fact that no hydrocarbons were detected in samples from Station 5 (9/80) indicates that the hydrocarbons observed in the other surface microlayer samples were due to droplets or patches of thin films of oil on the surface of the water and not due to soluble hydrocarbons in the surface micro-The variability in the concentrations of these compounds between duplicate samples tends to support this conclusion.

3.3.2 Phytoneuston and Detrital Particulate Density

Replicate subsamples of phytoneuston were enumerated at 100X magnification in a Palmer-Maloney chamber and detrital particles at 250X in a Hemacytometer chamber (Table 6).

The samples were dominated by pennate diatoms. Most taxa were similar to those described from Northwest marine microlayer samples previously described (Hardy, 1973; Hardy and Valett, 1981). Phytoneuston densities (55 to 2,400/ml) were much greater (probably 10X) than could be expected in the phytoplankton. The ciliate Mesodenium rubrum was present in all samples in low numbers and therefore was not quantified. Very dense particulate detrital material concentrations (20 x 10^3 to 122 x 10^3 /ml) occurred in the microlayer. Insufficient sample prevented the analysis of the material for halogenated organic compounds and aromatic hydrocarbons.

3.4 Chemical Analyses of Suspended Matter

3.4.1 General Screening of Suspended Matter Samples

In order to be able to focus our detailed chemical analysis efforts on major differences in the chemical compositions of suspended matter collected with depth from Hylebos Waterway (Station 5) and Blair Waterway (Station 8), we first qualitatively screened each suspended matter sample by GC analysis using a FID and EC detector. GC analysis of the suspended matter from the two stations using the FID detector revealed no major visual differences in gas chromatographic patterns. However, GC analysis employing an electron capture detector indicated significant differences in the distributions and levels of electron capturing components between stations and with depth. Figures 7 and 8 show representative gas chromatograms of aromatic hydrocarbon and electron capturing components isolated from suspended matter from Stations 5 and 8.

3.4.2 GC/MS Analyses of Organic Extracts of Suspended Matter for Organic Pollutants

Extracts of samples of suspended matter collected at a depth of 2 m from Stations 5 and 8 were used for GC/MS analyses. It was felt that this suspended material would be most representative of recent input to the water column of toxic substances in that its presence was least likely to have resulted from disturbance of bottom sediment. GC/MS analyses of the suspended matter from Stations 5 and 8 confirmed the presence of a wide range of aromatic hydrocarbons ranging in molecular weight from naphthalene to perylene. However, due to their low concentrations and lack of sufficient sample, chlorinated biphenyls were not detected even with the use of single-ion monitoring during mass spectrometric analysis although their presence was indicated based on GC retention time data employing an electron capture detector. Other halogenated organic compounds were detected in the suspended matter, some of which had spectral patterns similar to those reported in last year's report (Riley et. al., 1980); however, absolute structural assignments have not as yet been made to these Suspended matter samples containing high levels of electroncapturing components were also examined for the presence of some pesticides (lindane, dieldrin, heptachlor, aldrin, p,p'-DDD, p,p'-DDT, p,p'-DDE, endrin, methoxychlor, chlorinated benzenes). These compounds were not detected by single-ion monitoring, thus they were eliminated from further consideration in our quantification scheme.

3.4.3 Aromatic Hydrocarbons in Suspended Matter (Quantitative)

Tables 7 through 10 list the concentrations of a select group of aromatic hydrocarbons in suspended matter from Stations 5 and 8 as a function of depth and time of sampling. No statistically significant differences were observed between the mean average total aromatic hydrocarbon concentrations in suspended matter collected from Station 5 in September $(10,454 \pm 6,560)$ and December $(7,454 \pm 4,188)$ and at Station 8 in September $(7,157 \pm 6,101)$ and December $(6,703 \pm 3,303)$. Also, no statistically significant differences were observed in the mean concentrations of total aromatic hydrocarbons between stations.

However, there appeared to be a trend toward increased total concentrations of aromatic hydrocarbons in suspended matter collected near the surface (2 m) as opposed to near the bottom. The one discrepancy to this trend was found in a 9-m suspended matter sample taken from Station 8 in September. A possible explanation for this discrepancy would suggest possible disturbance of surface sediment at this site during the time of sampling. From our analysis of sediment cores, it was found that surface sediment at this site contained high concentrations of what appeared to be a petroleum distillate (see section on sediments). Total mean concentrations of the selected aromatic hydrocarbons with depth ranged from 3 ppm to 18 ppm with 45 to 57% of the aromatic mass associated with five of the eighteen aromatic hydrocarbons analyzed. These compounds were benzanthracene, chrysene, benz(e)pyrene, benz(a)pyrene and perylene These results are consistent with decreased susceptibility of (Table 11). these compounds (relative to 1-, 2-, and 3-ring aromatics) to chemical and biological modification during transport to bottom sediments. The value for the ratio of phenanthrene to anthracene for all samples of suspended matter analyzed was 4.2 + 1.9 (Table 12).

3.4.4 <u>Halogenated Organic Compounds in Suspended Matter (Quantitative)</u>

Tables 13 through 16 list the concentrations of a select group of halogenated organic compounds in suspended matter. Total concentrations of selected halogens was highest in suspended matter collected from Station 5 during the December sampling and lowest at Station 8 for both sampling cruises. concentrations at Station 8 were lower by approximately 50 to over 100 times relative to the concentrations observed in suspended matter collected at Station 5 during the December cruise. Total selected halogen concentrations in suspended matter collected from Station 5 during the September cruise was lower by a factor of about 4 relative to the concentrations measured in suspended matter collected from Station 5 during the December cruise. No significant differences in the total selected halogen concentrations were observed with depth in suspended matter collected from Station 8 during both sampling cruises. A similar observation was made for the high concentrations of total selected halogens isolated from suspended matter collected from Station 5 during the December cruise. However, samples collected from Station 5 during the September sampling cruise had elevated concentrations of total selected halogen in suspended matter collected near the surface (2 m). Concentrations of individual chlorinated butadienes and chlorinated biphenyls followed a similar trend as observed for the total selected halogen concentrations.

3.5 Sediment Chemistry

3.5.1 Qualitative Organic Analysis of Sediments (GC/MS)

In order to determine the range and concentrations of organic compound types present in the sediment cores from the various locations in the two waterways, we screened extracts of the sections of the sediment cores using capillary gas chromatography employing flame ionization and electron capture detectors. This preliminary screen showed the presence of four classes of organic compounds which, based on our limited analysis scheme, appeared to encompass the major classes of compounds that were present in the cores.

The majority of sediment core sections contained a range of polyaromatic hydrocarbons (naphthalene to perylene in molecular weight range) with the highest concentrations appearing in one of the replicate core samples collected from Station 7 (Fig. 9). Surface sediment from the core collected from Station 8 contained high concentrations of naphthalene isomers most likely associated with a weathered petroleum distillate (Fig. 9). The sediment cores collected from Stations 5 and 6 contained high levels of Cl₁ to Cl₅ chlorinated biphenyls (Figs. 10 and 11). The characterization and quantification of chlorinated biphenyls in core 5 were confirmed by the NMFS Analytical Laboratory, Seattle, as part of an intercomparison study (see Section 3.9). In addition to chlorinated biphenyls, cores 2, 3, 5 and 6 contained chlorinated butadienes with the highest concentrations appearing in core 6 (Figs. 10 and 11). The chlorinated butadienes consisted of at least two major components which corresponded to two trichlorinated butadiene isomers whose class identities were confirmed by GC/MS (Fig. 12). Sediment samples containing high levels of electron-capturing components were also examined for the presence of some pesticides (lindane, dieldrin, heptachlor, aldrin, p,p'-DDD, p,p'-DDT, p,p'-DDE, endrin, methoxychlor, chlorinated benzenes). These compounds were not detected by single-ion monitoring and thus were eliminated from further consideration in our quantification scheme. PCBs containing seven or more chlorine atoms were not detected; the Cl6 biphenyls were present in only trace quantities. These compounds were also eliminated from further consideration in our quantification scheme.

Based on this preliminary assessment, samples of sediment from each core were analyzed and individual components (previously described, see General Analytical Strategy, 2.3) of the compounds described above were quantified by capillary gas chromatography. These data are listed in Tables 19 through 44 and will be discussed in detail in later sections of this report.

3.5.2 Estimation of Sediment Age (137Cs and 210pb Dating)

The data used to estimate sediment age are the relative activities of 137 Cs, 210 Pb, % organic carbon and grain size in the 11 sediment cores collected at the 10 stations. Generally there is a good correlation between the increased organic carbon, increased content of fine sediment (silt and clay), and increased 210 Pb and 137 Cs. That relationship is due to the radionuclides being associated with fine grained, organically rich, and high surface area sediment. The radionuclide data have been normalized to 40 K to eliminate variations in size of sediment pellets and variations between gamma detectors. The 40 K activity per gram dry weight of sediment is uniform ($^{15\%}$, 15 S.D.) over all the sediment samples and is used as an internal standard. Potassium- 40 K is a natural, long-lived (half life - $^{1.3}$ x 109 years) radionuclide present in the sediment minerals.

Cesium-137 (^{137}Cs) is a fission product radionuclide present in surface sediments as the result of fallout from atmospheric testing of nuclear weapons. The major ^{137}Cs fallout occurred between 1958 and 1965. The rate of ^{137}Cs fallout during the last 5 to 8 year period is approximately one-fifth the rate during the early 1960's (Robbins and Edgington, 1975). The half life of 137 Cs is 30 years, so more than half of the 137 Cs is still present in the environment. The 137 Cs distribution expected to be present in a continuously accumulating sediment core would have a subsurface 137 Cs maximum below which 137 Cs should decrease to below detection levels. This 137 Cs profile has been observed in a Lake Washington sediment core (Fig. 13) collected in the mid-1970's approximately 40 km from Commencement Bay. The Lake Washington 13 /Cs sediment profile is an example of sediments that are accumulating at a rate of almost $\dot{1}$ cm per year and receive very little sediment reworking. The ^{137}Cs profiles from Central Puget Sound are markedly different from that of Lake Washington. An example is a profile from East Passage (between Seattle and Tacoma) that shows fairly uniform $^{137}\mathrm{Cs}$ activity to a depth of 50 cm (Fig. 13). This featureless profile is interpreted as vigorous reworking and sedimentation of >2 cm per year that results in no subsurface maximum, just a uniform distribution the length of the core. The core from East Passage was not long enough to recover sediments not contaminated with 137 Cs. Therefore, greater than 50 cm of the sediments in East Passage contain contaminant that entered Puget Sound during the last 25 years. The presence of $^{137}\mathrm{Cs}$ is used to indicate sediments that have been contaminated with anthropogenic materials during the last 25 years. The absence of $^{137}\mathrm{Cs}$ indicates either no contaminants have accumulated in the sediments during the last 25 years or the sediment was deposited more than 25 years ago and has not been contaminated with more recent materials.

Lead-210 is a natural decay product of the 238 U decay series. Most of the 210 Pb in Puget Sound sediments is believed to have come from the decay of 222 Rn in the atmosphere. Lead-210 has a residence time in Puget Sound water of not more than several months before it deposits in the sediments. The half life of 210 Pb is 22 years. Thus, the activity of 210 Pb in sediment which came from the atmosphere (also called unsupported Pb) will decrease by a factor of 2 for every 20 years the sediment layer has been removed from the sediment water surface. If sediment mixing occurs, then more unsupported 210 Pb will be mixed into the older, deeper sediments, possibly resulting in an interpretation of higher than actual sedimentation rates. A second continuous source of 210 Pb to the sediments is supported 210 Pb, that which is present in equilibrium with the decay of 238 U present in the minerals. Supported 210 Pb activity is assumed to be constant with depth in a core and is usually taken to be the relatively uniform activity measured at depth in a core below the depth of unsupported 210 Pb activity. The expected activities of 137 Cs and 210 Pb in surface Puget Sound, fine-grained sediments are 0.5 to $^{2.0}$ dpm/g for 137 Cs and 5 to 10 dpm/g for 210 Pb. These values would agree with those reported by Schell and Nevissi (1977) and Bennett (1980). When converted to 137 Cs/ 40 K and 210 Pb/ 40 K ratios, values in the range of 0.2 to 0.8 and 0.4 to 0.8, respectively, would be expected in surface sediment.

The following is our interpretation of the last several decades of history of the 11 sedimentary cores and the corresponding data on the concentrations of aromatic and halogenated organic compounds in these cores. Tables 17 and 18 lists general chemical and physical data used in the interpretation of sediment age. Age dates have been added to several profiles (see Figs. 14, 16 and 18). However, these ages are approximate and are our best estimate based on the available data. For several cores, ages were not estimated because the radionuclide profiles were not easily interpreted.

3.5.3 History of Sedimentary Cores

3.5.3.1 Hylebos Waterway

Station 1 (Core 1) - Upper Turning Basin, Hylebos Waterway. Both ^{137}Cs and ^{210}Pb levels decrease with depth from the surface to that of the 15 to 20 cm layer (Fig. 14). This layer (0 to 20 cm) is the sediment contaminated during the last 25 years. Below 20 cm ^{137}Cs is not detected and ^{210}Pb is at the supported level. The texture of the core changed from black mud in the 0 to 20 cm layer to grey clay including some sand below 20 cm. The sediment below 20 cm may be the bottom of the dredged channel and be greater than 50 years old.

The concentrations of a select group of individual PAH in this core ranged from 7,098 $\mu g/kg$ to 354 $\mu g/kg$. The concencentrations of the select group of PAH (benzanthracene to perylene) decreased in an exponential fashion with depth (Fig. 14, Table 19) correlating well with the possible age of the sediment. Conceivably, this profile could represent a sediment area recently subjected to dredging activites. Trace levels of chlorinated butadienes (5 to 52 $\mu g/kg$, not plotted, see Table 20) were detected with depth in this core with the highest concentrations appearing near the surface. With the exception of trace levels in the surface sediment, chlorinated biphenyls were not detected in this core (Table 20).

Station 2 (Core 2) - Lower Turning Basin, North Side of Channel Cesium-137 is present throughout the core, indicating the sediments are less than 25 years old. The decrease in ^{137}Cs and ^{210}Pb that occurs at the 5 to 10 cm layer is due to a decrease in organic carbon. The black mud in the upper 30 cm of the core transformed to sand and gravel in the 30 to 42 cm layer. The sand and gravel are assumed to be the results of dredging operations. Concentrations of specific PAH (Fig. 14, Table 21) ranged from 167 to 6,697 $\mu\text{g/kg}$. The concentrations of PAH with depth were random which would support the age of the sediment and an impact due to dredging activities. Concentrations of halogenated organics with depth were also random and ranged from 403 to 1317 $\mu\text{g/kg}$ for chlorinated butadienes and 31 to 203 $\mu\text{g/kg}$ for selected chlorinated biphenyls (Fig. 15, Table 22).

These compounds were selected in the monitoring of aromatic hydrocarbons because they were in areas of the chromatograms void of interferences from halogenated organic compounds, thus their quantification is accurate. This compensation had to be made due to the high concentrations of PCB's in Core 5 and Core 6.

Station 3 (Core 3) - Central Hylebos Waterway, South Side of Channel. The sediment was relatively uniform mud throughout. Both ^{137}Cs and ^{210}Pb increased at the bottom of the core (Fig. 14). Age of the bottom of the core must be less than 25 years old. Concentrations of selected PAH ranged from 287 to 14,582 $\mu\text{g/kg}$ (Fig. 14, Table 23) and increased with increased sediment depth. Concentrations of chlorinated butadienes ranged from 627 to 1,072 $\mu\text{g/kg}$ with the highest concentrations appearing at a sediment depth of 5 to 15 cm. Total selected chlorinated biphenyl concentrations ranged from 196 to 2,456 $\mu\text{g/kg}$ with the concentrations of these components, as with the PAH, increasing with increasing sediment of depth (Fig. 15, Table 24). Assuming the sediment at this sampling station has been relatively undisturbed, the above results would suggest a major input of PAH and chlorinated biphenyls about 25 years ago.

Station 4 (Core 4) - Central Hylebos Waterway, North Side Subtidal Flat. This sandy core had relatively low carbon content except for the bottom of core which contained mud. Only a trace of ^{137}Cs was present in the upper 10 cm of the core and ^{210}Pb was at near supported levels in the entire core. This location does not appear to be an active contaminant accumulation site. Concentrations of selected PAH ranged from 6 to 505 $\mu\text{g/kg}$ with the highest concentrations occurring in the top 10 cm. However, concentrations of PAH did increase somewhat at the bottom of the core which correlates with the bottom of the core containing mud (Fig. 14, Table 25). Both chlorinated butadienes (272 $\mu\text{g/kg})$ and chlorinated biphenyls (154 $\mu\text{g/kg})$ were found in the surface sediment (0 to 5 cm) of this core but dropped off to just above or below detection limits at greater depths (not plotted, see Table 26).

Station 5 (Core 5) - Lower Hylebos Waterway, South Side. Black mud was present for the entire core. Both ^{210}Pb and ^{137}Cs were elevated the entire length with ^{137}Cs showing a significant subsurface peak at the 15 to 20 cm depth. The core represents less than 20 years of accumulation. Concentrations of individual select PAH in this core ranged from 137 to 3,038 $\mu\text{g/kg}$ (Fig. 16, Table 27). No significant trend in the concentrations of individual PAH with sediment depth was observed. The concentrations of chlorinated butadienes ranged from 2,154 to 4,057 $\mu\text{g/kg}$ and the concentrations of selected chlorinated biphenyls ranged from 383 to 4,051 $\mu\text{g/kg}$. The distribution pattern for the chlorinated biphenyls in this core fit that of Arochlor 1242. The highest concentrations of chlorinated butadienes were detected at a sediment depth of 0 to 15 cm; whereas the highest concentrations of chlorinated biphenyls were detected at a depth of 5 to 20 cm (Fig. 17, Table 28). These results combined with the age of the sediment suggest that a pulse of chlorinated biphenyls was deposited in the sediments about 25 years ago and that a steadily increasing accumulation of chlorinated butadienes has been occurring over the same period of time.

Station 6 (Cores 6) - Lower Hylebos Waterway, South Side of Channel. This muddy core had increases in both ^{137}Cs and ^{210}Pb with depth indicating the sediments may have been disturbed. The subsurface maximum in ^{137}Cs could be due to the maximum fallout of the 1960's but ^{210}Pb should not increase with depth. The age of the core bottom is probably less than 20 years. The

concentrations of selected PAH in this sediment core ranged from 28 to 1,764 $\mu g/kg$ with no apparent trend in their concentrations with sediment depth (Fig. 16, Table 29). The concentrations of chlorinated butadienes ranged from 17,818 to 77,098 $\mu g/kg$ and were the highest levels detected in all cores analyzed. Concentrations of specific chlorinated biphenyls range from 1,057 to 7,272 $\mu g/kg$. The highest concentrations for both classes of compounds were observed at a depth of 5 to 15 cm indicating a pulse of input of these components to this area in the past 20 years (Fig. 17, Table 30).

Station 7 (Core 7 and Core 7, duplicate) - Commencement Bay, Between the Two Duplicate cores (3 m apart) were collected at this station to obtain some information regarding the variability between replicate cores and to attempt to obtain information on sedimentation rate in an area not believed to have been dredged. The agreement between the cores is remarkably good with respect to grain size, organic carbon and radionuclides. The profile of ^{137}Cs shows the subsurface maximum indicating sediment mixing is not very extensive at this station. Also the ^{210}Pb decrease with depth is in agreement with ^{137}Cs indicating the 30 cm of core have been deposited in approximately the last 25 years (Fig. 16). The concentrations of selected PAH in the duplicate sediment core varied, especially at sediment depths greater than 15 cm. Concentrations of PAH in the first sediment core ranged from 17 to 3,425 µg/kg and for the duplicate core from 150 to 13,942 µg/kg (Tables 31 and 32, respectively). The reasons for this variability could have been influenced by several factors such as high variability in pollutant input, differences in sample core compaction during sample collection, and a non-parallel stratification of PAH in the sediment core. Concentrations and sample variability of chlorinated butadienes and chlorinated biphenyls were low at all depths. Concentrations ranged from 19 to 83 μ g/kg for chlorinated butadienes and from 19 to 42 μ g/kg for chlorinated biphenyls from one core and from 26 to 85 μ g/kg and <39 to 58 $\mu g/kg$, respectively, for the duplicate core (Tables 33 and 34, respectively).

3.5.3.2 Blair Waterway

All three cores from Blair Waterway had basically similar profiles for ^{137}Cs and ^{210}Pb , fairly low levels and generally only slight changes with depth. Blair Waterway appears to be accumulating low organic carbon sediments from the Puyallup River. The turbid river plume is often observed near the entrance to Blair. The relatively low ratio of ^{137}Cs and ^{210}Pb to ^{40}K indicates that old sediments (greater than 25 years) are accumulating in Blair Waterway, or that dredging has removed much of the sediment deposited in the last several decades, leaving a mixed layer of older sediments. The most probable interpretation is that sedimentation is rapid ($^{\sim}2$ cm/year) in much of Blair Waterway as the result of Puyallup River sediment which would be low in carbon ^{137}Cs , and ^{210}Pb , thus accounting for the level observed.

Station 8 (Core 8) - Lower Blair Waterway, North Side of Channel. Both ^{137}Cs and ^{210}Pb increase at the bottom of the core. The ^{137}Cs increase may be due to the maximum fallout from early 1960's, thus an age of 15 years could be assigned to the bottom of the core. Concentrations of selected PAH in this

sediment core ranged from 10 to 1,848 $\mu g/kg$. Concentrations of these components were highest at the bottom of the sediment core (Fig. 18, Table 35) and decreased to a minimum as one traversed upward to the center of the core. The concentrations of selected PAH increased substantially at the top of the sediment core. This increase was attributed to a recent input of narrow boiling point hydrocarbons consisting mainly of naphthalenes. This trend was further confirmed by comparison of the concentrations of selected naphthalenes between sediment cores from all stations and core 8 (0-5 cm depth). Concentrations of these aromatics in Core 8 (0-5 cm depth were from 7- to 50-times higher (Table 36) than in all other core sections. These components most likely resulted from a petroleum distillate spill or discharge. For the most part, the concentrations of halogenated organic compounds were below detectable levels (Table 37).

Station 9 - Central Blair Waterway, North Side of Channel. Both ^{137}Cs and ^{210}Pb exhibited little change with depth in this core. No indication was present for a subsurface ^{137}Cs maximum which could have possibly been removed by dredging. Concentrations of PAH were relatively low ranging in this sediment core from 32 to 1,066 $\mu\text{g/kg}$ with individual component concentrations decreasing with increasing depth (Fig. 18, Table 38). Only trace levels of halogenated organic compounds were detected (Table 39).

Station 10 - Blair Waterway, Turning Basin. Both ^{137}Cs and ^{210}Pb decreased with depth in this case with ^{137}Cs almost reaching the detection limit. The bottom of the core must be approximately 25 years old. The concentrations of selected PAH ranged from 8 to 493 $\mu\text{g/kg}$ with the concentrations of individual PAH decreasing with increasing depth. The concentrations of many of the aromatic hydrocarbons were below the limits of detection at the greatest depth of 30-40 cm (Fig. 18, Table 40). Only trace levels of halogenated organic compounds were detected in sediment from this core (Table 41).

3.6 Waterway Profile of Total Selected Aromatic Hydrocarbons in Sediments

Figure 19 shows the profile for the concentrations of total aromatic hydrocarbons as a function of sediment depth and station. Concentrations of total aromatic hydrocarbons varied considerably from station to station with the highest concentrations appearing at Stations 3 and 7. Due to the limited sampling size, these distributions should not be taken as the absolute profile for the aromatic hydrocarbon distributions in these waterways. This point is further exemplified by the potential for incidence of high variability in the total aromatic hydrocarbon concentrations as observed in the duplicate samples analyzed from Station 7. The duplicate core sections analyzed from depths of 0 to 5 cm, 5 to 10 cm, 10 to 15 cm and 20 to 30 cm had total aromatic hydrocarbon concentration variability ranging from 6 to 17%. This is in contrast to the core sections at a depth of 15 to 20 cm which had a variability of 102%, which is a result of elevated levels of aromatic hydrocarbons from fluorene to perylene in one of the duplicate samples (see Tables 31 and 32).

3.7 Phenanthrene/Anthracene Ratios in Sediments

Table 42 lists the ratio of phenanthrene/anthracene for sediments collected from both waterways. About half of the sediment sections showed ratios that ranged from 2.4 to 5.4. However, cores 1, 2, 3, 4, 9 and 10 showed ratios that for the most part were less than 2 and appeared in some cases to decrease with increased depth. The ratios in these cores (1, 2, 3, 4, 9, 10) also appeared to be lower than the ratios observed in suspended matter (Table 12).

3.8 Waterway Profile of Total Selected Chlorinated Butadienes and Chlorinated Biphenyls in Sediments

Figure 20 shows the profile for the concentrations of total selected chlorinated butadienes and chlorinated biphenyls as a function of station location and sediment depth. The highest concentrations of chlorinated butadienes and chlorinated biphenyls were associated with sediments collected from Stations 5 and 6. Concentrations at these stations were in the range of 10 to 1,000 times higher than at the other stations with the exceptions of sediments from Stations 2 and 3 where the concentrations of these component classes ranged from 403 to 1,072 $\mu g/kg$ for chlorinated butadienes and 31 to 2,456 $\mu g/kg$ for chlorinated biphenyls.

3.9 Distribution of Selected Aromatic Hydrocarbons Between Water, Suspended Matter and Surface Sediment

We did not quantify selected aromatic hydrocarbons in filtered water as a part of this study because they have been shown, for the most part, to be present at levels that are below the detection limits of the XAD-2 resin method (Riley et al., 1980). However, in order to obtain more information regarding the distribution of these compounds between water, suspended matter and sediment, we needed this type of data. It is believed that a good estimation of the distributions could be made by combining the water data obtained in last year's study (Riley et al., 1980, page 51) with data from this study on suspended matter and surface sediment. The surface sediment and suspended matter used in the comparison was obtained from Station 5 in September 1980. The water data were obtained at approximately the same location in September 1979. These data are listed in Table 43.

The concentrations of total selected aromatic hydrocarbons were present at levels less than 0.041 $\mu g/l$. In contrast, concentrations of total selected aromatic hydrocarbons in suspended matter and sediment were 11,086 $\mu g/kg$ and 9,604 $\mu g/kg$ respectively. These concentration differences resulted in distributions of aromatic hydrocarbons that were approximately 100,000 times higher in suspended matter and sediment than in filtered water. It appears that the average percent distribution of total aromatic hydrocarbons for suspended matter and sediment to be about the same (53.6% vs 46.4%).

3.10 Distribution of Selected Halogenated Organic Compounds Between Water, Suspended Matter and Surface Sediment

Table 44 lists the concentrations and distributions of a select group of halogenated organic compounds between water, suspended matter and surface sediment. Data for suspended matter and surface sediment were from the same samples used above (Section 3.9) except the water data was taken from Table 13 of this study.

Concentrations of chlorinated butadienes in water ranged from 4 to 252 μ g/l. In suspended matter, the concentrations of chlorinated butadienes ranged from 8 to 1,677 μ g/l and in sediment from 7 to 2,731 μ g/l. The Cl₁ to Cl₃ chlorinated biphenyls ranged in concentration from 3 to 317 μ g/l. The Cl₄ and Cl₅ chlorinated biphenyls were not detected in the water. Concentrations of Cl₁ to Cl₅ chlorinated biphenyls ranged from 184 to 4,950 μ g/l and in sediment the range was from 62 to 301 μ g/l.

Unlike the aromatic hydrocarbons, several of the chlorinated butadienes and chlorinated biphenyls produced distributions which reflected greater hydrophilicity. These compounds included Cl₃-butadiene-1, hexachlorobutadiene and the Cl₁ to Cl₅ chlorinated biphenyls. The reason for the low water distribution for Cl₃-butadiene-2 in unknown.

3.11 Sedimentation Rates

The interpretation of sedimentation rates and ages of sediments is complicated by disturbance of sediments due to dredging, other sediment mixing processes, and changes in sediment texture. Of the 11 sediment cores examined, the cores taken from Station 7 showed a $^{137}\mathrm{Cs}$ subsurface maximum and a decrease in $^{210}\mathrm{Pb}$ with depth in agreement with $^{137}\mathrm{Cs}$. The $^{137}\mathrm{Cs}$ profiles in Station 7 cores are similar to that observed in undisturbed sediments of Lake Washington (Fig. 13) and in Lake Michigan (Robbins and Edgington, 1975). These data, coupled with the fact that this sampling location appears to be out of the area of previous dredging activity, made it the best candidate for estimation of sedimentation rates in the area. Based on data from this core, the sedimentation rate in this area is estimated at $\sim\!0.7$ cm/year.

3.12 Input Rates of Selected Organics to Sediments in Hylebos and Blair Waterways

To gain a better understanding of the current impact of organic contaminants, we attempted to estimate the yearly input of some individual and selected classes of organic compounds to the sediments in Hylebos and Blair Waterways. From an Army Corps of Engineers map, the surface area of the main channels of Hylebos and Blair Waterways were estimated to be $\sim 4,670,000$ sq ft and 6,430,000 sq ft, respectively. Table 45 lists the input of selected organics to Hylebos and Blair Waterways assuming an average sedimentation rate of 0.7 cm/year (estimated from Station 7 sediment core profiles), an average

water content of 50% (from the ratioing of sediment dry wt to wet wt) for the sediment, and average concentrations of selected organics in suspended matter from Stations 5 and 8 (Tables 7-16). Total selected hydrocarbon input (naphthalene to perylene) to Hylebos and Blair Waterways was estimated to be 13.7 kg/year, respectively. Input rates of benzanthracene benz(a)pyrene were estimated to be 0.7 and 0.6 kg/year for Hylebos Waterway and 0.4 and 0.2 kg/year for Blair Waterway. The estimated rate of input for the sum of the two trichlorobutadiene isomers was 2.8 kg/year for Hylebos Waterway and 0.2 kg/year for Blair Waterway. The estimated rate of input of hexachlorobutadiene was 0.06 kg/yr for Hylebos Waterway and 0.01 kg/yr for Blair Waterway. The input of chlorinated biphenyls (Cl_1 to Cl_5) was estimated at 189 kg/year for Hylebos Waterway and 21 kg/year for Blair Waterway. It is felt that the estimates given for the input rates of total aromatics, benzanthracene, and benz(a)pyrene are reasonable based on the similarities in concentrations for these components detected in suspended matter from Stations 5 and 8 and the fact that these components are well represented in all the sediments analyzed from the two waterways. On the other hand, the input rate for trichlorobutadienes must be viewed with caution since the estimation is based on their concentrations in suspended matter from Stations 5 and 8 which have been shown to vary considerably in the concentrations of these components. estimate of chlorinated biphenyl input to the waterways has to be viewed with caution also, especially the value estimated for Hylebos Waterway. Since we only measured 5 selected chlorinated biphenyl components in the suspended matter from Station 5 for which we know there are at least 30 major components detected by mass spectrometry in the corresponding sediment, our extrapolation to a total chlorinated biphenyl concentration in suspended matter from Stations 5 and 8 in itself is an estimate. In addition, as for the trichlorbutadienes, variability in the concentrations of chlorinated biphenyls in suspended matter from Stations 5 and 8 as a function of sampling time was high.

3.13 Intercomparison Study

Table 46 lists the results of the Battelle and NOAA/NMFS analyses of sediment from Core 5 (10-15 cm) in Hylebos Waterway for the presence of chlorinated biphenyls. Both laboratories showed that the sediment contained Cl₁ through Cl₅ chlorinated biphenyl isomers. Both laboratories indicated the total concentrations of chlorinated biphenyls to be quite high (553 µg/g vs $150~\mu g/g$). It is felt that the 3- to 4-fold difference in the total concentrations observed between the two labs can be attributed to the analysis of heterogeneous samples. These results are also consistent with the observed variability in the concentrations of these components in sediment core 5 with depth (see Section 3.5.3.1) from which the intercomparison samples were derived.

4. DISCUSSION

The purpose of this study was to gain a better understanding of the historical and current inputs and the distributions of organic pollutants to Hylebos and Blair Waterways located adjacent to Commencement Bay in Puget Sound, near the city of Tacoma. To evaluate these parameters we examined, on the basis of a limited analytical scheme coupled with age dating techniques ($^{137}\mathrm{Cs}$, $^{210}\mathrm{Pb}$), the chemistry of the organic compounds associated with sediment, suspended matter and water from these two waterways collected during two sampling cruises in September and December 1980. Chemical analyses of sediment cores indicated the historical input of three major classes of organic These classes of compounds were aromatic hydrocarbons (2 to 5 rings), chlorinated biphenyls (Cl₁ to Cl₅) and chlorinated butadienes. distribution pattern for the chlorinated biphenyls in the most concentrated sediment fit that of Arochlor 1242. The concentrations of these compounds varied with sampling location and sediment depth by as much as three orders of magnitude. Comparison of the organic chemistry of our surface sediment data to the surface chemistry data obtained by the National Marine Fisheries Service at locations corresponding closely to our stations indicated reasonable agreement in concentrations of compounds and classes of compounds found in these sediments (Malins et al., 1980). However, this study shows that evaluation of the distributions and impact of organic toxicants at specific sites can be seriously underestimated if sampling is limited to the examination of only surface sediments.

Age dating indicated that most of the sediments fell into two categories consisting of recent disturbed sediments (<25 years) and what appeared to be older (>25 years) undisturbed sediments. For the most part, the older sediments contained the lowest concentrations of organic compounds with the highest concentrations appearing near the surface, suggesting that most contaminated sediments had previously been removed as a result of dredging activities or that the areas were areas of high accumulation with uncontaminated particulate material.

Due to differences in reactivity (National Academy of Sciences, 1972) and solubility (May et al., 1978), the ratio of phenanthrene/anthracene has recently been used to provide some insight into the environmental modification of PAH. Sources of anthropogenic aromatic hydrocarbon pollutants (i.e., fuel oil, crankcase oils, soots and tars) have been shown to contain ratios of phenanthrene/anthracene in the range of 8 to 50 (Lake et al., 1979; Giger and Shaffner, 1978). A lower ratio observed in environmental sediments and suspended matter suggests a preferential transformation of phenanthrene and other aromatic hydrocarbons with similar susceptibility due to impact from chemical and biological degradation processes. Examination of sediment cores from Narragansett Bay showed phenanthrene/anthracene ratios to be relatively low and constant (3.0 to 4.3, Lake et al., 1979). Most sediment core samples from this study as well as the suspended matter had phenanthrene/anthracene ratios that fell within this same range. The fact that the ratios in suspended matter were similar to most ratios in sediments suggests that biological and chemical processes acting on aromatic hydrocarbons up to three rings following deposition in bottom sediments is slow. On the other hand, cores, 1, 4 and 10 contained sediment near the bottom of the core with phenanthrene/anthracene ratios of less than 1 indicating that these sediment processes produce changes that occur over periods of 15 to 20 years of time or that an increase in the chemical complexity of the insult due to anthropogenic sources of aromatic hydrocarbon input to these sediments have increased substantially in recent years.

Some sediment cores contained areas of very high concentrations of chlorinated biphenyls (cores 5 and 6), trichlorobutadienes (cores 5 and 6) and aromatic hydrocarbons. The extent in the size of these hot spot areas could not be determined due to the limited sampling size. In addition, many of the sediment cores did not reach the bottom of the sediment bed; thus, total mass of sediment in the waterways could not be estimated and organic chemical budgets for the individual or classes of compounds detected in these sediments could not be determined.

Examination of the distributions of a selected group of aromatic hydrocarbons and halogenated organic compounds between water, suspended matter and sediment indicated suspended matter and sediment were good sinks for the aromatic hydrocarbons. However, significant amounts of the chlorinated butadienes and the low molecular chlorinated biphenyls (Cl $_1$ through Cl $_3$) were present in the water column, which suggests that these compounds need to be examined further with respect to potential human health effects and impact to pelagic organisms.

Age dating of sediment cores collected from a location in Commencement Bay and between the mouths of the two waterways (Station 7) showed good correlation between ^{137}Cs and ^{210}Pb permitting the use of these cores in estimating the rate of sedimentation in this area. From these cores, a value of 0.7 cm/year was calculated in good agreement with and well within the range of sedimentation rates (0.1-2.0 cm/year) previously measured in different regions of Puget Sound (Schell and Nevissi, 1977) but somewhat less than the rates of 1.5 to 1.7 cm/year measured in the tidal Hudson River, New York (Bopp et al., 1981), and considerably less than the 10 to 20 cm/year measured in dredged areas of New York Harbor (Olsen, et al., 1978).

Analysis of suspended matter and water (filtered, nonfiltered and surface microlayer) indicated these compartments to contain these same classes of compounds indicating a continued input of these contaminants to bottom sediments. Table 42 indicates that input rates of aromatic hydrocarbon to Blair Waterway are equal to or somewhat less than input rates to Hylebos Waterway. However, evidence presented earlier in this report would suggest that the annual input rates to Blair Waterway are underestimated due to high rates of sedimentation of "clean" sediment resulting from impact by the plume of the Puyallup River. We did not account for this influence in our estimates. Thus, it is possible that Blair Waterway is accumulating aromatic hydrocarbons at a faster rate than Hylebos Waterway.

The influence of the Puyallup River could also explain the differences in the halogenated organic chemical composition of suspended matter and sediments collected from Station 5 near the mouth of Hylebos Waterway and Station 8 near the mouth of Blair Waterway. The concentrations of halogenated organic compounds in suspended matter and sediment from Station 5 were significantly higher than from Station 8. These data suggest that the action of the plume of the Puyallup River, in effect, significantly reduces the transport and subsequent deposition of Hylebos Waterway suspended matter to Blair Waterway. data would also suggest that the source of these components in suspended matter and water (as disrupted sediment and/or recent discharge) is located near the mouth of Hylebos Waterway. These results are also in agreement with respect to the relative amounts and types of halogenated organic compounds found in suspended matter collected from the same general station location the previous year (Riley et al., 1980). It is interesting to note that the concentrations of trichlorobutadienes appeared to be highest in filtered water collected at Stations 5 and 6. Concentrations of these components dropped off significantly at Station 7 but increased again at Station 8. The major difference in the chlorinated butadiene chemistry between Stations 5 and 8 was that the highest concentrations of the compounds appeared to be near the surface (2 m) at Station 5 but near the bottom (9 m) at Station 8. At this time, we have no explanation for the latter observation.

Both waterways contained detectable levels of haloforms and other low molecular weight chlorinated and non-chlorinated volatile organics most of which are on the Environmental Protection Agency toxic substances list. source of these pollutants could be direct discharge, at least in this case of the haloforms, from chemical transformations resulting from the release of active chlorine to the waterways. Previous researchers have reported on studies related to the formation of halogenated compounds from the low level chlorination of natural waters (Jolley et al., 1978; Bean et al., 1980; Carpenter and Smith, 1978). Many of these halogenated organic compounds are known or suspected carcinogens or mutagens (Jolley et al., 1978) and a most recent study has indicated that while some of these compounds are degraded under anaerobic experimental conditions, no aerobic conditions could be found that resulted in their degradation (Bouever et al., 1981). This same study showed trichloroethylene and tetrachloroethylene to be resistant to both aerobic and anaerobic degradation processes which suggests these compounds, as well as the major volatile component (1, 1, 1-trichloroethane), found in these waterways, may accumulate in sediments.

The data in this report tend to support the hypothesis that several classes of organic compounds have impacted Hylebos and Blair Waterways in the past 25 years. Fluxes of these classes of compounds continue to persist. Once these pollutants are incorporated into sediments, it appears that mechanical processes (dredging activities) and natural processes (biological degradation) have minimal impact on decreasing the persistence of these components in the sediments of these waterways.

RECOMMENDATIONS

The Commencement Bay area of Puget Sound is highly industrialized. Recent studies (Riley et al., 1980; Malins et al., 1980) and this study have shown that water, suspended matter, and sediments from areas of the bay and adjacent waterways are contaminated with both organic and inorganic anthropogenic toxicants. Increased frequencies of tumors and lesions have been observed in fish and invertebrate species residing in this area. However, it has been shown that further research is needed to establish possible cause-and-effect relationships between these contaminants and the corresponding biota.

Past strategies for the disposal of contaminated sediments from waterways adjacent to Commencement Bay (Hylebos and Blair Waterways) have included transport and disposal to central areas of Commencement Bay and to above ground landfill sites adjacent to the bay. The soundness of these disposal practices is unknown in light of the fact that little is known about the potential release of organic and inorganic toxicants from these disposal sediments as a result of prolonged leaching and underwater desorption processes. A logical extension of this study would be to conduct research to gain a better understanding of the extent of release of specific classes of organic toxicants to Puget Sound waters as a result of engaging in these two types of disposal practices. The goal of the project would be to evaluate the previous impacts and relative potential environmental impact associated with continued practice of these disposal strategies.

In addition to the above goal, a continued effort should be directed toward characterization and quantification of organic toxicants at sites of intensive industrial development adjacent to Puget Sound. Our chemical studies in Hylebos and Blair Waterways have indicated the presence of halogenated organic compounds in suspended matter whose chemical structures are still unknown at this time. An effort should be made to identify these compounds as well as other suspect compounds (i.e., chlorinated phenols) and assess their environmental impact.

Our study has shown Hylebos and Blair Waterways, due to past dredging activities, to vary considerably in the level of polluted sediment associated with a specific waterway site. Because, in many cases, our cores never reached to unimpacted sediments, a pollutant mass budget for these waterways was not obtainable. Additional cores taken in strategic areas of the waterways at greater depths would provide the information necessary to permit a mass budget assessment.

Our study also produced sediment cores which appeared to contain preindustrial sediments. Characterization and quantification of organic components associated with these sediments would provide a better understanding of the overall impact of industrialization on Puget Sound.

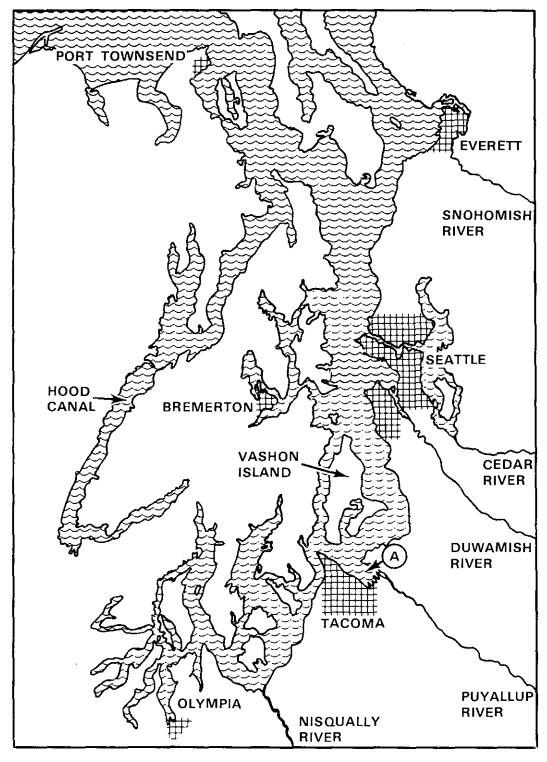


Fig. 1. General Map Showing the Location of Commencement Bay (A)

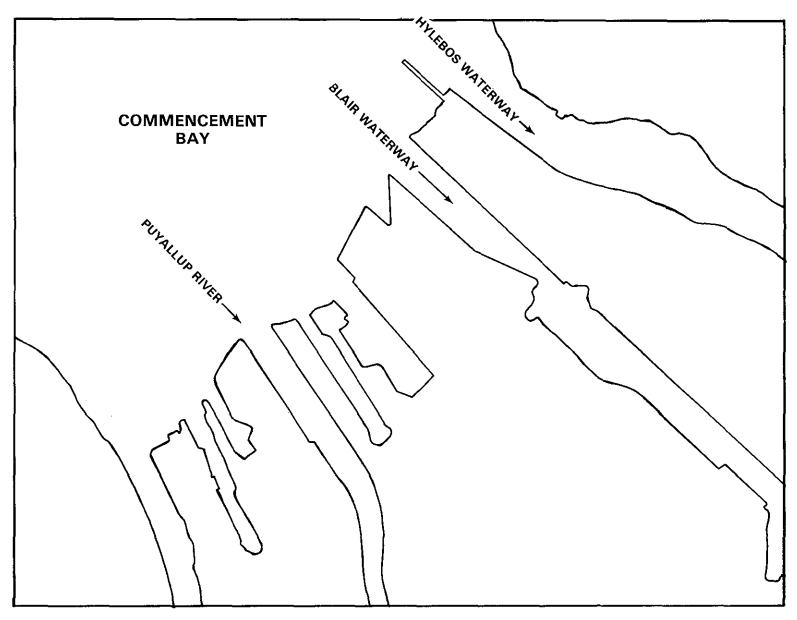


Fig. 2. Map of Commencement Bay Area Showing Location of Puyallup River, Hylebos Waterway and Blair Waterway

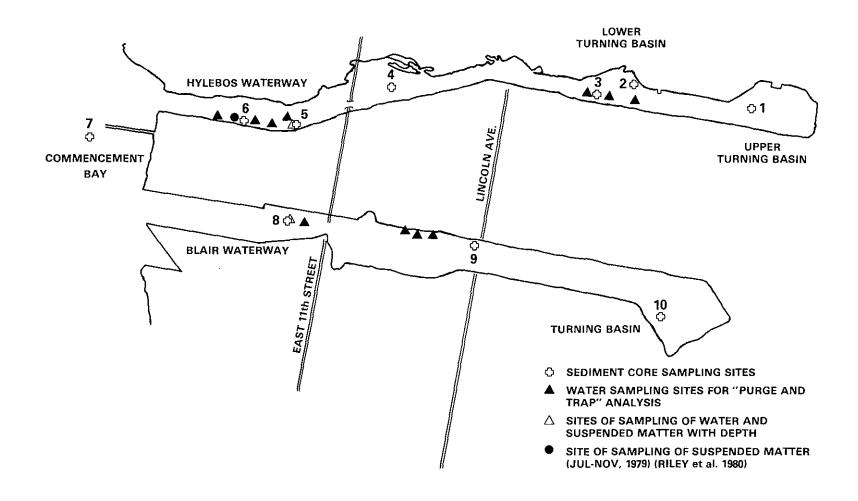


Fig. 3. Sampling and Sampling Type Locations

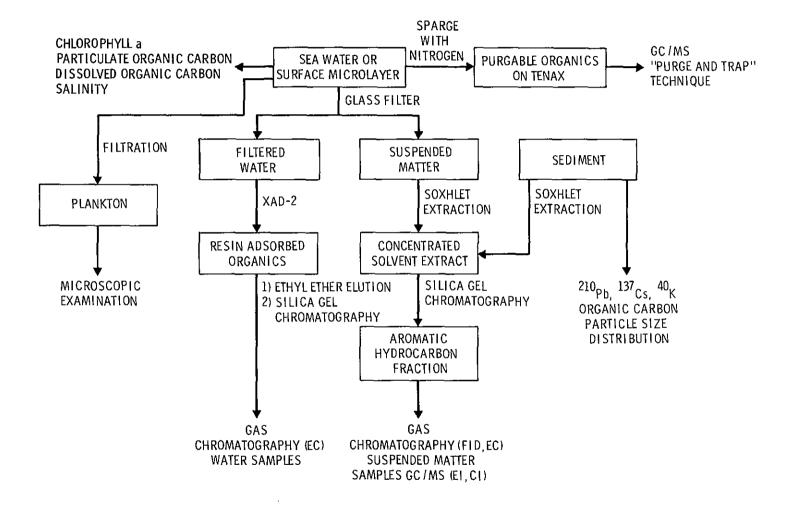
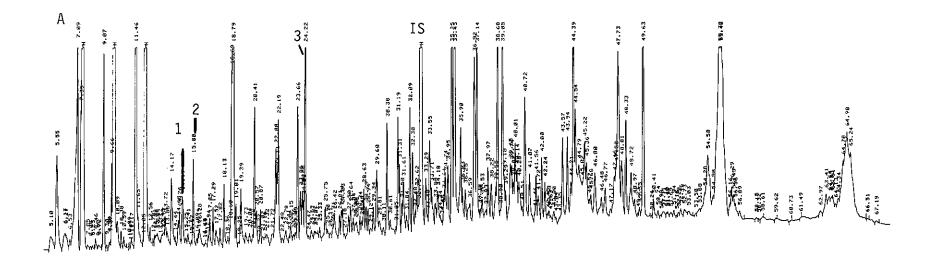


Fig. 4. General Sampling and Analytical Scheme





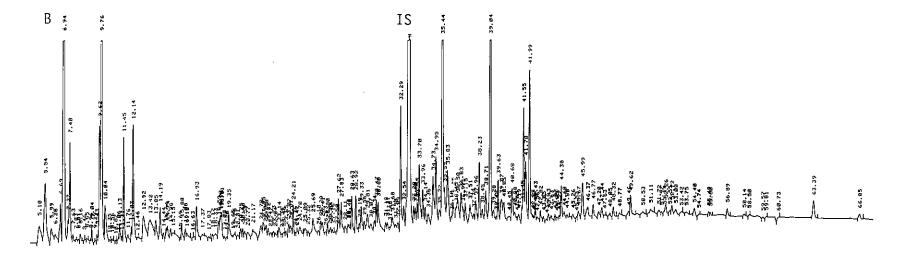


Fig. 5. GC Chromatograms Depicting Electron Capturing Components Isolated from Water (2 m depth) from (A) Station 5 and (B) Station 8 in December 1980. IS = 2-bromonaphthalene internal standard. (1) = trichlorobutadiene isomer-1, (2) = trichlorobutadiene isomer-2 and (3) = hexachlorobutadiene

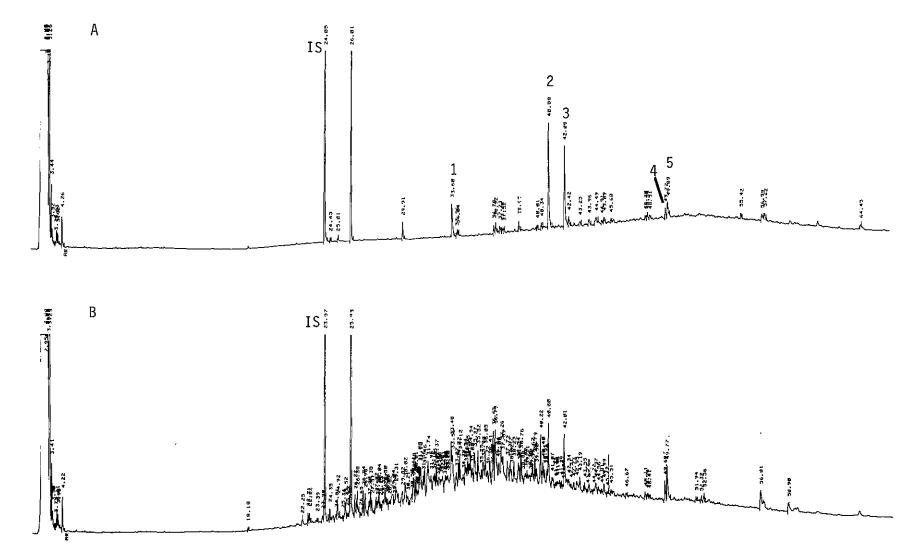


Fig. 6. GC Chromatograms Depicting Aromatic Hydrocarbon Components Isolated from the Surface Microlayer at (A) Station 5 and (B) Station 8 in December 1980. IS = hexamethylbenzene internal standard. (1) = phenanthrene, (2) = fluoranthene, (3) = pyrene, (4) = benzanthracene, and (5) = chrysene



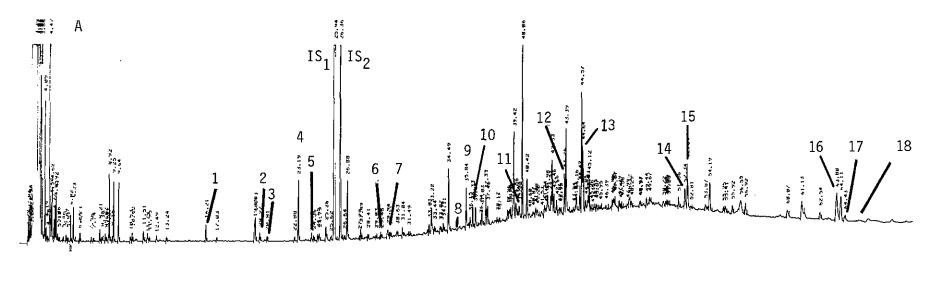
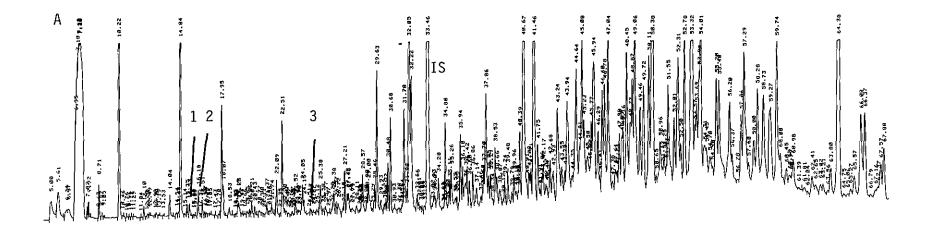




Fig. 7. GC Chromatograms Depicting Aromatic Hydrocarbon Components Isolated from Suspended Matter (2 m depth) from (A) Station 5 and (B) Station 8 in December 1980. IS₁ = hexamethylbenzene internal standard, IS₂ = 2-bromonaphthalene internal standard. (1) = naphthalene, (2) = 2-methylnaphthalene, lene, (3) = 1-methylnaphthalene, (4) = biphenyl, (5) = 2,6-dimethylnaphthalene, (6) = 2,3,5-trimethylnaphthalene, (7) = fluorene, (8) = dibenzothiophene, (9) = phenanthrene, (10) = anthracene, (11) = 1-methylphenanthrene, (12) = fluoranthene, (13) = pyrene, (14) = benzanthracene, (15) = chrysene, (16) = benz(e)pyrene, (17) = benz(a)pyrene, and (18) = perylene



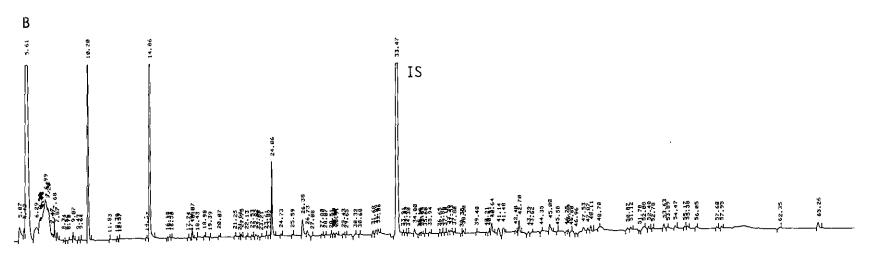
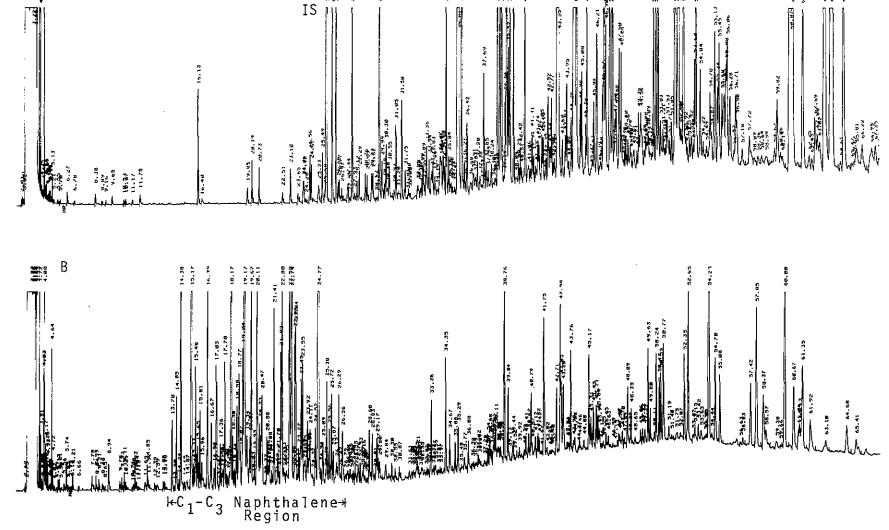


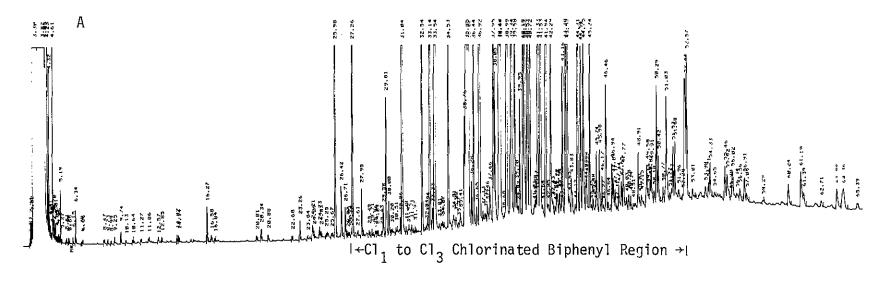
Fig. 8. GC Chromatograms Depicting Electron Capturing Components Isolated from Suspended Matter (2 m depth) from (A) Station 5 and (B) Station 8 in September 1980. IS = 2-bromonaphthalene internal standard. (1) = trichlorobutadiene isomer-1, (2) = trichlorobutadiene isomer-2, and (3) = hexachlorobutadiene





25.83 26.24 26.54

Fig. 9. GC Chromatograms Depicting Aromatic Hydrocarbon Components Isolated from Sediment from (A) Station 7 (15-20 cm, duplicate) and (B) Station 8 (0-5 cm). IS = hexamethylbenzene internal standard. Note naphthalene region



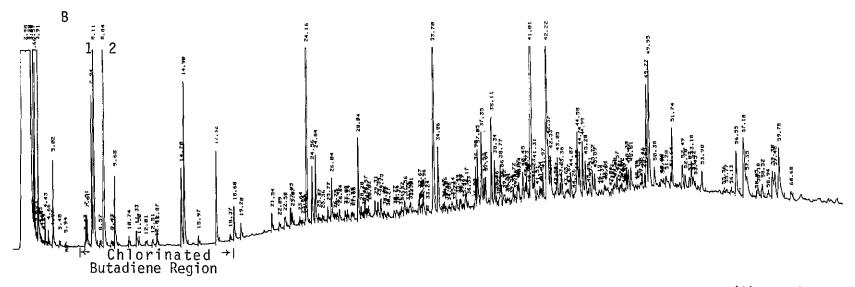
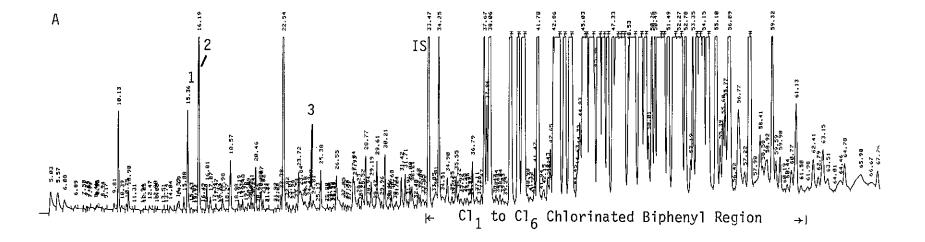
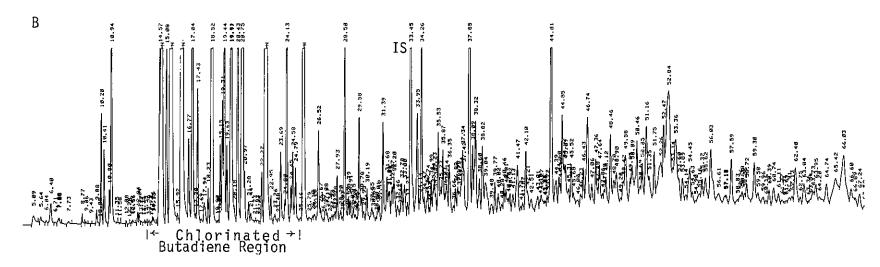


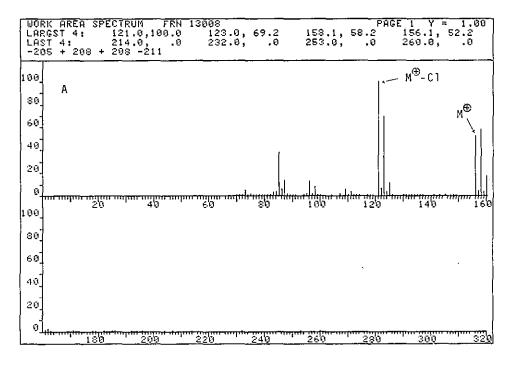
Fig. 10. GC Chromatograms Showing FID Response of Components Isolated from Sediment from (A) Station 5 (10-15 cm) and (B) Station 6 (15-20 cm). IS = hexamethylbenzene internal standard. Note chlorinated biphenyl and chlorinated butadiene regions. (1) = trichlorobutadiene isomer-1 and (2) = trichlorobutadiene isomer-2





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Fig. 11. GC Chromatograms Depicting Electron Capturing Components Isolated from Sediment from (A) Station 5 (10-15 cm) and (B) Station 6 (15-20 cm). IS = 2-bromonaphthalene internal standard. Note chlorinated biphenyl and chlorinated butadiene regions. (1) = trichlorobutadiene isomer-1, (2) = trichlorobutadiene isomer-2, and (3) = hexachlorobutadiene



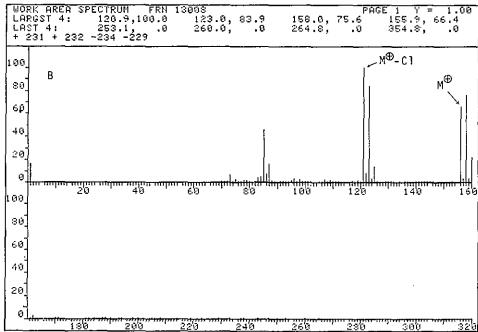


Fig. 12. Mass Spectra of Trichlorobutadiene Isomers. (A) = trichlorobutadiene-1 and (B) = trichlorobutadiene-2

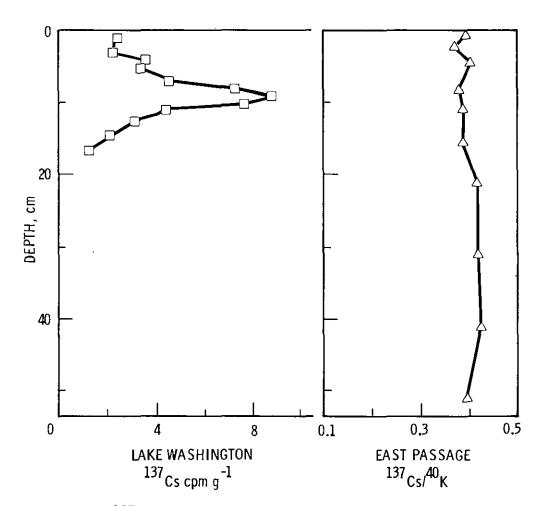


Fig. 13. ^{137}Cs Profiles of Sediment Cores from Lake Washington and East Passage

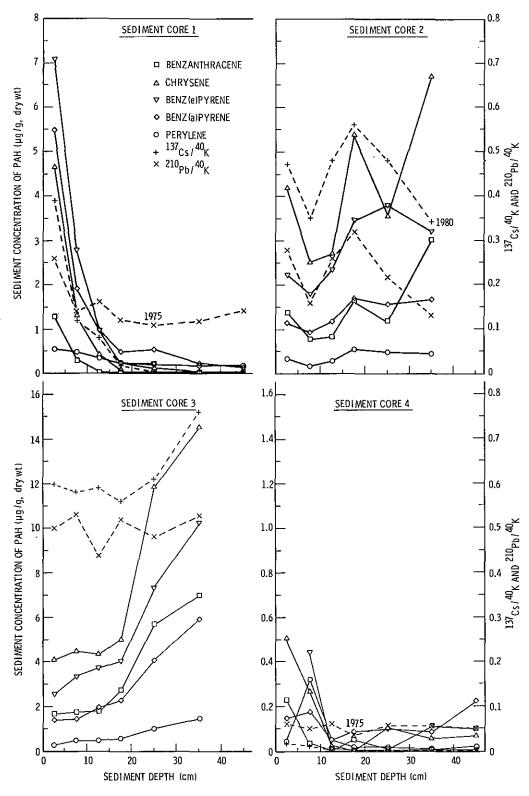


Fig. 14. PAH Concentrations and Dating Profiles for Sediment Cores 1 through 4

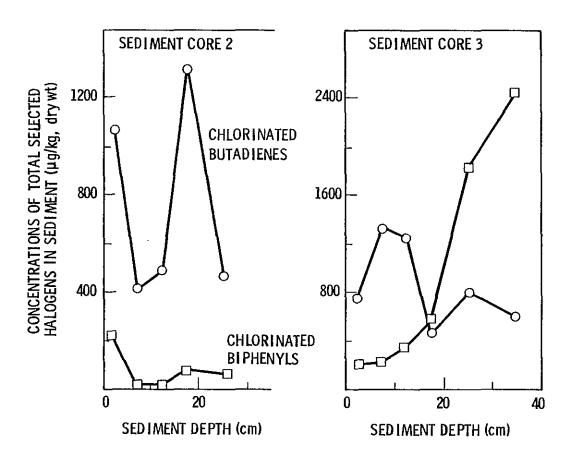


Fig. 15. Concentrations of Total Selected Chlorinated Biphenyls and Chlorinated Butadienes in Cores 2 and 3 as a Function of Sediment Depth

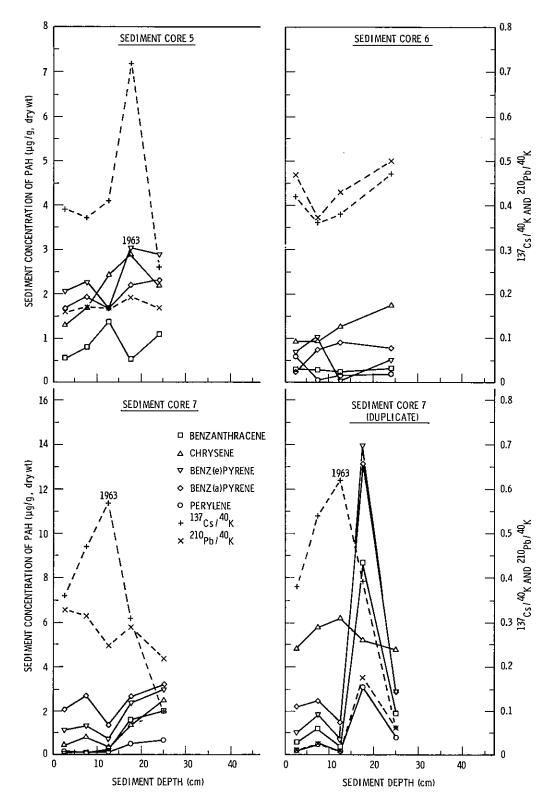


Fig. 16. PAH Concentrations and Dating Profiles for Sediment Cores 5-7

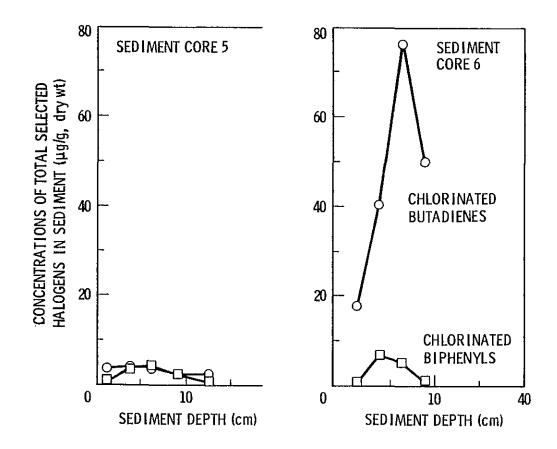


Fig. 17. Concentrations of Total Selected Chlorinated Biphenyls and Chlorinated Butadienes in Cores 5 and 6 as a Function of Sediment Depth

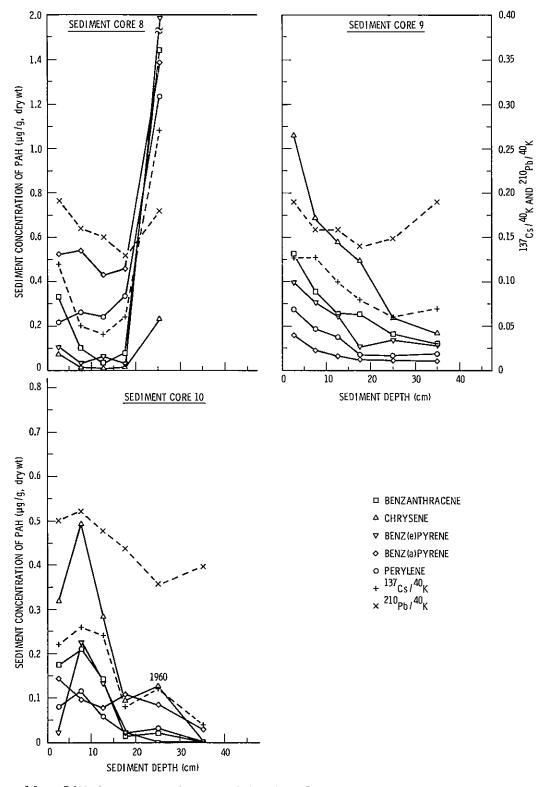


Fig. 18. PAH Concentrations and Dating Profiles for Sediments Cores 8-10

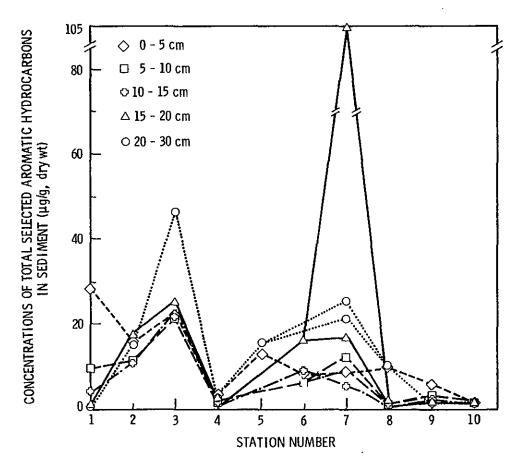


Fig. 19. Concentrations of Total Selected Aromatic Hydrocarbons as a Function of Sediment Depth and Station. Note: Two samples were taken at Station 7 to show sample-to-sample variation

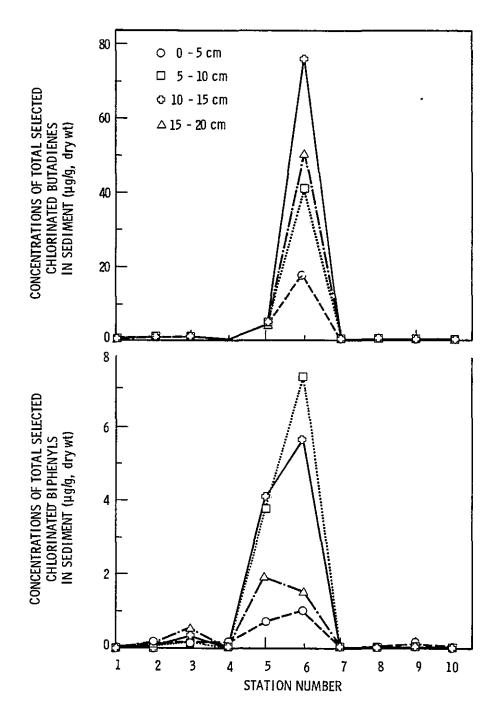


Fig. 20. Concentrations of Total Selected Chlorinated Butadienes and Chlorinated Biphenyls as a Function of Sediment Depth and Station

Table 1. Physical and Chemical Parameters for Hylebos and Blair Waterways - September 1980

Station Location	Sample Depth (m)	Temperature (C°)	Salinity (°/∞)	Suspended Load (mg/l dry wt)	% Organic C ¹ (dry wt)	DOC ² (mgC/1)	POC ³ (mgC/1)	Chlorophyll A (mg/m ³)	Volume Filtered (1)
Hylebos Waterway	5A						· • · ·		
9/9/80	2	20	27.4	3.2	6.9	1.18	0.22	1.01	1,565
	5	14	29.6	3.4	3.2	1.29	0.11	0.65	2,264
	9	14	29.9	4.4	2.5	1.02	0.11	0.60	1,283
Hylebos Waterway	<u>58</u>								
9/11/80	2	16	24.6	2.1	11.9	1.50	0.25	2.47	1,245
	5	14	29.1	3.2	3.1	1.06	0.10	0.73	2,420
	9	14	29.9	9.4	2.7	0.85	0.25	0.79	2,006
Blair Waterway 8	<u>4</u>								
9/10/80	2	16	26.5	7.5	4.1	1.16	0.31	1.89	1,358
	5	14	29.6	5.1	1.8	0.84	0.09	0.85	2,858
	7	14	-	7.4	1.8	0.96	0.13	0.78	1,540
Blair Waterway 81	3.								
9/10/80	2	16	26.4	5.3	-	-	-	1.49	1,118
	5	14	29.3	5.6	2.1	0.93	0.12	0.61	1,387
	9	13	29.7	5.8	1.6	0.96	.09	0.62	1,665

 $^{^{1}}_{2}\%$ organic carbon (dry wt) content of suspended matter. $^{3}_{90C}$ = dissolved organic carbon. $^{3}_{P0C}$ = particulate organic carbon.

Table 2. Physical and Chemical Parameters for Hylebos and Blair Waterways - December 1980

Station Location	Sample Depth (m)	Temperature (C°)	Salinity (°/ ₀ ,)	Suspended Load (mg/l dry wt)	% Organic C ¹ (dry wt)	DOC ² (mgC/1)	POC ³ (mgC/1)	Chlorophyll A (mg/m ³)	Volume Filtered (1)
Hylebos Waterway	5A								
12/15/80	2	11	26.5	2.3	6.1	2.02	0.14	0.39	1,923
	5	11	29.0	2.5	5.6	1.28	0.14	0.22	3,764
	9	11	29.9	2.5	4.4	1.34	0.11	0.16	2,632
Hylebos Waterway	<u>5B</u>								
12/15/80	2	11	27.6	3.1	9.0	-	0.28	0.20	1,783
	5	11	28.7	2.0	10.0	-	0.20	0.23	3,464
	9	11	30.0	3.5	7.4	0.96	0.26	0.26	2,352
Blair Waterway 8A									
12/16/80	2	11	28.5	2.3	7.0	0.94	0.16	0.24	1,932
	5	11	29.8	2.0	3.5	0.85	0.07	0.24	3,515
	9	11	29.9	3.3	3.0	0.82	0.10	0.21	3,028
Blair Waterway 88									
12/17/80	2	10	27.3	2.9	4.1	1.74	0.12	0.22	1,639
	5	11	29.8	1.9	6.8	0.91	0.13	0.18	4,183
	9	11	30.0	5.9	2.4	0.97	0.14	0.30	2,581

Table 3. Concentration ($\mu g/l$, \bar{x} \pm range) of Volatile Hydrocarbons in Water Collected from Blair and Hylebos Waterways

		Suspect Discha	rge near Stati	on 3 (9/9/80)	(12/15/80)	(12/15/80)
Compound	B1ank	Below	Adjacent	Above	Station 5	Station 8
methylene chloride	3.1 <u>+</u> 1.8	9.5 ± 0.9 $(6.4 \pm 0.9)^{1}$	$ \begin{array}{c} 11.7 \pm 0.5 \\ (8.6 \pm 0.5) \\ 1.7 \end{array} $	$ \begin{array}{c} 14.7 \pm 5.1 \\ (11.7 \pm 5.1) \end{array} $	$\begin{array}{c} 7.2 \pm 0.2 \\ (4.1 \pm 0.2) \\ 3.8 \end{array}$	4.5 ± 0.5 $(.14 \pm 0.4)$
1,2-dichloroethylene chloroform 1,2-dichloropropane	0.2	0.5 ± 0.9	1.7 - 2.8 ± 0.7 0.2	1.6 <u>+</u> 0.4	3.8 - 2.3 <u>+</u> 0.4	0.4 ± 0.1
dichlorobromomethane 1,1,1-trichloroethane trichloroethylene benzene	0.1 0.6 2.8 <u>+</u> 1.7	$\begin{array}{c} 0.9 \\ 0.6 + 0.2 \\ 1.4 + 1.3 \end{array}$	0.2 0.7 + 0.1 1.5 + 1.2	1.1 + 0.2 1.3 + 0.9	41-1 + 0.8 3.8 + 0.2 1.9 + 2.5	20.4 ± 2.5 0.2 2.0 ± 2.4
dibromochloromethane bromoform 1,1,2,2-tetra-		(0) 0.2 1.5 ± 0.2	(0) ⁻ 0.3 <u>+</u> 0.3	(0) 0.3	(0.5 ± 0.6) 0.6 ± 0.1	(0.5 ± 0.6)
chloroethane tetrachloroethylene toluene	0.2	0.3 <u>+</u> 0.0	$\begin{array}{c} 0.7 \pm 0.6 \\ 0.4 \pm 0.1 \end{array}$	0.3	$\begin{array}{c} 1.1 \pm 0.3 \\ 0.6 \pm 0.1 \\ 0.3 \end{array}$	0.2 0.3 <u>+</u> 0.1
Total Volatiles ²		11.6 <u>+</u> 0.4	13.5 <u>+</u> 0.8	14.3 <u>+</u> 5.3	53.9 <u>+</u> 0.8	22.9 + 2.8

	Bank	Seep near Stati (12/15/80)	on 9	Suspect Discharge near Station 6 (12/15/80)				
Compaund	Below	Adjacent	Above	Below	Adjacent	Above		
methylene chloride 1,2-dichloroethylene	2.0 <u>+</u> 1.0 (0)	4.7 ± 2.6 (1.7 ± 2.4)	$\begin{array}{c} 3.6 \pm 2.6 \\ (1.2 \pm 1.7) \end{array}$	$\begin{array}{c} 3.6 \pm 0.0 \\ (0.5 \pm 0.0) \\ 0.7 \end{array}$	$\begin{array}{c} 6.9 \pm 1.1 \\ (3.8 \pm 1.1) \\ 1.3 \end{array}$	$\begin{array}{c} 3.9 \pm 0.4 \\ (0.8 \pm 0.4) \\ 0.3 \end{array}$		
chloroform 1,2-dichloropropane dichlorobromomethane	0.4 <u>+</u> 0.1	0.3 <u>+</u> 0.1	0.4 <u>+</u> 0.2	2.2 <u>+</u> 0.0	1.8 ± 0.1	2.2 <u>+</u> 0.1		
1,1,1-trichloroethane trichloroethylene dibromochloromethane	33.1 + 7.4	33.5 <u>+</u> 4.1 0.1	33.5 <u>+</u> 4.2	$\begin{array}{c} 30.0 \pm 4.9 \\ 0.7 \pm 0.3 \end{array}$	$\begin{array}{c} 28.7 \pm 3.6 \\ 0.7 \pm 0.1 \end{array}$	31.8 ± 5.3 0.7 0.1 + 0.1		
benzene bromoform	2.5 ± 0.3 (0) 0.7	(0.5 ± 0.6)	$\begin{array}{c} 3.1 \pm 1.4 \\ (0.6 \pm 0.6) \end{array}$	$\begin{array}{c} 1.5 + 1.9 \\ (0.0 + 0.0) \\ 1.0 + 0.5 \end{array}$	$\begin{array}{c} 1.6 \pm 1.8 \\ (0.1 \pm 0.1) \end{array}$	$\begin{array}{c} 1.9 \mp 2.3 \\ (0.2 \mp 0.3) \\ 1.3 + 0.6 \end{array}$		
1,1,2,2-tetra- chloroethane						· -		
tetrachloroethylene toluene	0.2 ± 0.1 0.4 ± 0.2	0.1 3.4 <u>+</u> 2.9	12.5 <u>+</u> 4.5	$\begin{array}{c} 0.2 \pm 0.2 \\ 11.2 \pm 12.5 \end{array}$	$\begin{array}{c} 0.2 \pm 0.1 \\ 15.7 \pm 9.5 \end{array}$	0.3		
Total Volatiles	36.0 <u>+</u> 8.4	39.4 <u>+</u> 3.9	48.0 <u>+</u> 9.9	49.0 <u>+</u> 17.3	51.0 <u>+</u> 14.2	36.4 <u>+</u> 5.2		

² Values in parentheses exclude concentrations found in blank.

Concentrations reported include the summation of only those values where duplicate values are available. For methylene chloride and benzene, the effect of background has been subtracted.

Concentrations (ng/l, pptr) of Selected Halogenated Organic Compounds in Waters Collected from Hylebos and Blair Waterways Table 4.

		(1	C)		Total Selected		Chlorin	ated bip	nenyls		Total Selected
Station	Depth (meters)	Cl ₃ - Butadiene-l	Cl ₃ - Butadiene-2	HCBD ¹	Chlorinated Butadienes	C1 ₁	c1 ₂	c13	C1 ₄	cı ₅	Chlorinated Biphenyls
			Sep	tember 198	30 Sampling Crui	se	- -		-		
1 2 3 4 5	2.0 2.0 2.0 2.0 2.0 5.0	53 69 78 96 252 28 <2	81 55 9 65 <10 51 <2	9 7 1 11 4 13	143 131 88 172 256 92	82 45 98 98 317 68 49	28 33 10 1 220 61 42	3 2 <2 2 3 1 <1	1 1 <1 <1 <2 1 <1	<1 <1 <2 <1 <2 <1 <1	114 81 108 101 540 131 91
6 7 8	2.0 2.0 2.0 5.0 9.0	69 <2 <2 55 124	118 <2 3 <13 17	17 6 2 <1	204 6 5	79 93 120 125	60 80 34 <13	2 1 2 <2	<1 <1 1 <2	<1 <1 <1 <2	141 174 157 125
9 10	2.0 2.0	71 25	17 13 3	2 3 1	143 87 29	154 110 102	<12 13 48	<2 1 3	<2 <1 1	<2 <1 <1	154 124 154
			 Dec	ember 1980	Sampling Cruis	e					
1 2 3 4 5	2.0 2.0 2.0 2.0 2.0 5.0 9.0	10 41 28 29 62 20 <8	<11 92 69 55 86 54 <9	<1 18 15 13 18 12	10 151 112 97 166 86 1	26 44 36 95 88 37 22	27 76 14 96 268 148 <8	6 10 6 8 24 7 <1	<2 <2 <1 1 1 <1 <2	<2 <1 <1 <1 6 <1 <2	59 130 56 199 387 192 22
6 7 8	2.0 2.02,3 2.03,4 5.02,3 5.03,4 9.02,3 9.03,4	42 14 5 8 3 5 43 28	61 24 12 <3 9 <2 12	14 4 2 1 2 <1 1	107 42 19 11 12 5 555 28	128 97 76 63 80 57 88 34	203 88 55 10 58 13 58 <3	25 6 7 4 4 1 2 <1	<1 1 <1 1 1 1 <1 <1	1 1 <1 <1 <1 <1 <1	357 192 139 77 143 72 148 34
9 10	2.0	19 3	54 12	<1 2 4	28 75 19	87 82	11 106	7 24	<1 1	<1 <1	105 212

 $[\]overline{\mbox{I}_{\mbox{HCBD}}}$ is abbreviation for hexachlorobutadiene.

 $^{^{2}\}mathrm{Top}$ column of two series coupled XAD-2 resin columns.

For hexachlorobutadiene collected at the 2-m level of Station 8, the amount retained on top column was 2 ng/l and on the bottom column 1 ng/l. Thus, if a third, forth and fifth column were coupled in the series, a total of 0.5, 0.25 and 0.13 ng/l would be retained on these columns, respectively. Therefore, the amount of hexachlorobutadiene retained by the top column would be estimated to be 2/(2 + 1 + 0.5 + 0.25 + 0.13) = 52%. This approach was used for calculation of retention of those components discussed in the text.

 $^{^{4}}$ Bottom column of two series coupled XAD-2 resin columns.

Table 5. Concentrations ($\mu g/1$) of a Select Group of Aromatic Hydrocarbons in Surface Microlayer

Compounds	Station 5 9/80		Station 5 12/80		Station 8 9/80		Station 8 12/80	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
biphenyl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2,6-dimethylnaphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2,3,5-trimethylnaphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	5.0	2.0
fluorene	<0.3	<0.2	<0.2	<0.2	<0.3	<0.2	2.9	3.2
phenanthrene	<0.2	<0.2	8.4	4.7	<0.2	3.6	21.0	45.8
anthracene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	12.9	43.2
1-methylphenanthrene	<0.3	< 0.2	0.8	<0.2	<0.3	0.5	32.1	55.4
fluoranthene	<0.2	<0.2	26.9	17.5	<0.2	5.5	12.6	41.6
pyrene	<0.3	<0.2	22.6	15.0	<0.3	3.5	5.9	19.8
benz anthracene	<0.4	< 0.4	3. 3	5.3	<0.4	0.7	6.2	3.1
chrysene	<0.4	< 0.3	6. 3	13.7	<0.4	2.5	15.3	0.8
benz(e)pyrene	<0.8	<0.8	<0.8	ND1	<0.8	<0.7	ND	<0.6
benz(a)pyrene	<0.7	<0.7	<0.8	ND	<0.7	<0.6	ND	<0.5
perylene	<0.6	<0.6	<0.6	ND	<0.6	3.38	ND	<0.4
Total Aromatics	<5.0	<4.6	68.3	56.2	<5.0	19.7	113.9	214.9
x			62.3 +	8.6			164.4 <u>+</u>	71.4

 $I_{\text{Peaks were detected in this region but they were not quantifiable.}}$

Table 6. Phytoneuston and Detrital Particulate Density in the Surface Microlayer

Sample #	Date	Phytoneuston (dominant)	Approximate Total Density individuals/ml Mean + S.D.	Detritus particles x 10 ³ /ml Mean <u>+</u> S.D.
5A	9/9/80	Navicula (Prorocentrum)	280 <u>+</u> 80	15 <u>+</u> 1
5 A	12/15/80	(Navicula) Cylindrotheca Lyngbya (Navicula spp.)	2,300 <u>+</u> 290	66 <u>+</u> 8
5B	9/11/80	(microflagellates) <u>Chroomonas</u> sp. <u>Skelotoneuma</u> sp.	55 <u>+</u> 25	20 <u>+</u> 7
5B	12/16/80	Melosira (Navicula) Lyngbya microflagellates Achnanthes Amphora	1,020 <u>+</u> 140	54 <u>+</u> 11
9A	9/10/80	Amphora Navicula Pheuro/Gyrosigma Melosira Cylindrotheca Chroomonas (Nitzschia longissima Prorocentrum	2,980 <u>+</u> 80	48 <u>+</u> 7
8A	12/16/80	(Navicula spp.) microflagellates Gymnodinium sp. Lyngbya sp. Cylindrotheca sp.	420 <u>+</u> 40	122 <u>+</u> 14
8B	9/10/80	(Navicula spp.) Gyro/Plueurosigma (microflagellates) Amphora sp.	95 <u>+</u> 15	36 <u>+</u> 3
8B	12/17/80	dinoflagellates <u>Melosira</u> sp.	860 <u>+</u> 120	108 <u>+</u> 10

Table 7. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Suspended Matter from Station 5 as a Function of Depth - September 1980

			Depth	(meters)		
Compound	2	2	5	5	9	9
naphthalene	242	1,158	321	299	431	29
2-methylnaphthalene	78	314	94	95	124	10
1-methylnaphthalene	<12	138	57	37	51	<3
biphenyl	492	1,153	359	461	406	250
2,6-dimethylnaphthalene	<17	111	30	29	42	<4
2,3,5-trimethylnaph-						
thalene	<15	88	38	19	34	< 4
fluorene	114	358	161	92	151	16
dibenzothiophene	<110	167	226	40	58	≤27 [.]
phenanthrene	554	1,664	600	414	564	66
anthracene	210	441	242	106	156	8
1-methylphenanthrene	1,002	1017	*T	264	886	96
fluoranthene	1,470	2,353	1,028	185	830	382
pyrene	3,457	2,120	170	681	686	1,146
benzanthracene	379	1,419	833	212	386	59
chrysene	964	2,562	1,173	587	675	190
benz(e)pyrene	4,845	3,998	1,415	2,617	2,888	1,624
benz(a)pyrene	175	2,052	418	181	224	97
perylene	365	712	329	43	171	<17
Total aromatics ²	14,347	21,825	7,495	6,319	8,763	3,973
x <u>+</u> range	18,086	± 5,288	6,907	+ 832	6,368 <u>+</u>	3,387

¹Overlapping peaks; could not quantify.

 $^{2\}bar{x} \pm SD$ for all six total aromatics concentrations was 10,454 \pm 6,560.

Table 8. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Suspended Matter from Station 5 as a Function of Depth - December 1980

			Depth	(meters)		
Compound	2	2	5	5	9	9
naphthalene	244	167	279	188	606	357
2-methylnaphthalene	74	73	93	69	147	87
1-methylnaphthalene	<20	27	36	18	68	45
biphenyl	340	546	186	127	335	226
2,6-dimethylnaphthalene	<29	<13	58	<10	37	10
2,3,5-trimethylnaph-						
thalene	<27	19	30	21	40	18
fluorene	95	86	105	48	164	92
dibenzothiophene	<188	<87	<77	<64	<115	<64
phenanthrene	473	390	80	221	750	378
anthracene	75	81	160	40	241	73
1-methylphenanthrene	179	199	570	138	444	105
fluoranthene	558	530	1,848	331	1,003	331
pyrene	1,398	1,000	1,374	359	1,071	506
benzanthracene	397	467	588	115	426	136
chrysene	970	937	964	257	904	272
benze(e)pyrene	7,861	2,733	3,882	12	1,142	349
benz(a)pyrene	769	133	763	112	130	836
perylene	<120	<55	<49	<41	<74	<58
Total aromatics 1	13,443	7,388	10,520	2,056	7,508	3,811
x̄ <u>+</u> range	10,416 +	4,282	6,288 +	5,985	5,660 +	2,614

 $[\]frac{1}{x}$ ± SD for all six total aromatics concentrations was 7,454 ± 4,188.

Table 9. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Suspended Matter from Station 8 as a Function of Depth - September 1980

			Depth	(meters)		
Compound	2	2	5	5	91	9
naphthalene	102	139	284	396	1,637	255
2-methylnaphthalene	24	22	63	93	309	68
1-methylnaphthalene	<5	<8	36	48	181	28
biphenyl	518	459	161	294	598	235
2,6-dimethylnaphthalene	30	50	21	27	81	40
2,3,5-trimethylnaph-						
thalene	<7	<11	14	21	63	16
fluorene	22	<11	64	51	389	55
dibenzothiophene	<49	<74	26	22	264	<45
phenanthrene	170	209	286	13	1,890	256
anthracene	28	73	83	47	[*] 547	62
1-methylphenanthrene	150	1092	78	202	361	200
fluoranthene	606	672	282	558	2,802	231
pyrene	997	1,424	349	90	2,433	281
benzanthracene	77	103	178	40	1,205	97
chrysene	234	281	282	85	1,928	166
benze(e)pyrene	2,203	2,068	650	874	2,948	3,886
benz(a)pyrene	63	56	58	63	1,155	104
perylene	<31	<47	44	<27	417	<29
Total aromatics ²	5,224	6,648	2,959	2,924	19,207	5,980
x + range	5,224 +	6,648	2,959	<u>+</u> 25	1,2594 ±	9,353

Sample taken nearest to surface sediment containing a suspected petroleum distillate.

 $^{^2\}bar{x}$ \pm SD for all six total aromatics concentrations was 7,157 \pm 6,101.

Table 10. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Suspended Matter from Station 8 as a Function of Depth - December 1980

		· · · · · · · · · · · · · · · · · · ·	Depth	(meters)		
Compound	2	2	5	5	9	9
naphthalene	139	204	294	595	228	256
2-methylnaphthalene	72	106	86	107	61	47
1-methylnaphthalene	<17	36	44	57	22	24
biphenyl	491	436	240	214	157	186
2,6-dimethylnaphthalene	45	<16	31	21	<10	29
2,3,5-trimethylnaph-						
tha lene	33	30	29	28	<9	12
fluorene	30	105	101	113	47	57
dibenzothiophene	<158	<104	< 80	<63	<64	<39
phenanthrene	484	605	528	615	240	262
anthracene	84	104	141	134	35	74
1-methylphenanthrene	195	285	352	406	91	135
fluoranthene	284	282	382	1,017	216	437
pyrene	1,160	1,100	751	705	320	965
benzanthracene	405	393	292	245	76	118
chrysene	1,163	913	633	426	173	245
benz(e)pyrene	6,911	2,845	4,339	1,245	828	842
benz(a)pyrene	211	239	151	118	143	59
perylene	<101	<66	<51	<40	<41	<25
Total aromatics 1	11,707	7,683	8,394	6,046	2,637	3,748
x <u>+</u> range	9,695 <u>+</u>	2,845	7,220 ±	1,660	3,193	<u>+</u> 786

 $[\]frac{1}{x}$ + SD for all six total aromatics concentrations was 6,703 + 3,303.

Table 11. Concentrations ($\mu g/kg$) of Selected PAH in Suspended Matter from Stations 5 and 8^{1}

Compound	Station 5 9/80	Station 5 12/80	Station 8 9/80	Station 8 12/80
benzanthracene chrysene benz(e)pyrene benz(a)pyrene perylene	548 + 499 $1,025 + 825$ $2,898 + 1,334$ $525 + 756$ $394 + 228$	355 + 189 717 + 351 2,662 + 2,941 457 + 365 <66 + 29	$ \begin{array}{r} 283 + 454 \\ 496 + 706 \\ 2,105 + 1,227 \\ 250 + 444 \\ 231 + 264^{2} \end{array} $	255 + 137 592 + 388 2,835 + 2,425 154 + 65 <54 + 27
Total PAH	5,258 <u>+</u> 3,093	4,189 <u>+</u> 3,485	3,210 <u>+</u> 2,463	3,836 <u>+</u> 2,935
% of Total Aromatics	50	56	45	57
$\frac{1}{1} \text{Total } \bar{x} \stackrel{+}{=} \text{rang}$ $2 \text{Total } \bar{x} \stackrel{+}{=} \text{rang}$				

Table 12. The Ratio of Phenanthrene/Anthracene in Suspended Matter

		Time of Sampling						
	Depth	9/8	80	12/80				
Station	(meters)	Rep 1	Rep 2	Rep 1	Rep 2			
5	2 5	2.6 2.5	3.8 3.9	6.3 0.5	4.8 5.5			
8	9 2 5 9	3.6 6.1 3.5 3.5	8.3 2.9 0.3 4.1	3.1 5.8 3.7 6.9	5.2 5.8 4.6 3.5			
⊼ <u>+</u> SD		3.6 <u>+</u> 1.3	3.9 <u>+</u> 2.6	4.4 <u>+</u> 2.4	4.9 <u>+</u> 0.8			

Table 13. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Suspended Matter from Station 5 as a Function of Depth - September 1980

			Depth (r	neters)	·	
Compound	2	2	5	5	9	9
Cl ₃ -butadiene-1	878	353	<21	<194	71	165
Cl ₃ -butadiene-2	2,870	483	<23	<220	96	451
HCBD	8	8	<3	<16	<4	<1
Cl ₁ -biphenyl	<28	184	<42	<372	28	<7
Cl ₂ -biphenyl	<160	881	62	<34	35	17
Cl ₃ -biphenyl	152	644	73	287	21	15
Cl ₄ -biphenyl	<4	4,950	13	<31	50	<1
Cl ₅ -biphenyl	475	1,310	34	10	21	2
Total chlorinated butadienes	3756	844	< 47	<430	167	616
Total chlorinated biphenyls	627	7,969	182	297	155	34
Total selected halogen ¹	4,383	8,813	182	297	322	650
⊼ <u>+</u> range	6,598	<u>+</u> 3,132	240	<u>+</u> 81	486 <u>+</u>	232

 $^{^{1}\}bar{x}$ \pm SD for all six total halogen concentrations was 2,441 \pm 3,515.

Table 14. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Suspended Matter from Station 5 as a Function of Depth - December 1980

		Depth (meters)						
Compound	2	2	5	5	9	9		
Cl ₃ -butadiene-1	357	123	322	462	981	1,055		
Cl ₃ -butadiene-2	1,140	<76	1,016	981	5,041	1,643		
HCBD	18	11	122	12	234	53		
Cl ₁ -biphenyl	<186	825	392	222	191	17		
Cl ₂ -biphenyl	846	1,034	574	771	442	335		
Cl ₃ -biphenyl	593	998	1694	880	577	143		
Cl ₄ -biphenyl	3,964	<11	4,421	3,227	2,538	821		
Cl ₅ -biphenyl	1,986	2,087	5,675	2,378	2,442	668		
Total chlorinated butadienes	1,515	134	1,460	1,455	6,256	2,751		
Total chlorinated biphenyls	7,389	4,944	12,756	7,478	6,190	1,984		
Total selected halogen1	8,904	5,078	14,216	8,933	12,446	4,375		
x̄ ± range	6,991	+ 2,705	11,575	± 3,736	8,411 <u>+</u>	5,707		

 $^{^{1}\}bar{x}$ \pm SD for all six total halogen concentrations was 8,992 \pm 3,895.

Table 15. Concentrations of Selected Halogenated Organic Compounds in Suspended Matter from Station 8 as a Function of Depth - September 1980

			Depth	(meters)		
Compound	2	2	5	5	9	9
Cl ₃ -butadiene-1	<10	30	26	31	52	50
Cl ₃ -butadiene-2	<12	10	89	113	104	109
HCBD	<2	<3	<1	<3	<4	2
Cl ₁ -biphenyl	61	<14	<δ	<10	<20	<31
Cl ₂ -biphenyl	<10	<7	<3	< 5	<12	<13
Cl ₃ -biphenyl	<2	3	4	5	8	<2
Cl ₄ -biphenyl	<2	3	6	<3	8	<2
Cl ₅ -biphenyl	<2	<3	<1	3	<4	<2
Total chlorinated butadienes	<24	40	115	144	156	161
Total chlorinated biphenyls	61	6	10	8	16	<50
Total selected halogen1	61	46	125	182	172	161
x <u>+</u> range	54 <u>+</u> 11		139	<u>+</u> 19	167	<u>+</u> 8

 $^{^{1}\}bar{\text{x}}$ $^{+}$ SD for all six total halogen concentrations was 120 $^{+}$ 54

Table 16. Concentrations of Selected Halogenated Organic Compounds in Suspended Matter from Station 8 as a Function of Depth - December 1980

			Depth (r	neters)		
Compound	2	2	5	5	9	9
Cl ₃ -butadiene-1	<100/	295	100	83	42	60
Cl ₃ -butadiene-2	<114	<265	<40	<88>	186	20
HCBD	· <10	21	6	<5	2	3
Cl ₁ -biphenyl	<196	<463	<68	<151	16	<21
Cl ₂ -biphenyl	<109	<253	<40	<83	<2	<12
Cl ₃ -biphenyl	133	<42	71	38	22	4
Cl ₄ -biphenyl	494	<42	<6	<13	2	<1
Cl ₅ -biphenyl	152	<42	57	<13	22	5
Total chlorinated butadienes	<224	316	106	83	130	83
Total chlorinated biphenyls	779	<842	128	38	62	9
Total selected halogen 1	779	316	234	121	292	92
		~				
x̄ <u>+</u> range	548 -	<u>+</u> 327	178 -	<u>+</u> 80	192 -	<u>+</u> 141

 $^{^{1}\}bar{x}$ \pm SD for all six total halogen concentrations was 306 \pm 249.

Table 17. Activity of ^{137}Cs and ^{210}Pb in Sediment Cores Normalized to ^{40}K and Total Organic Carbon (% dry wt) in Sediment Cores

Station Number	Depth (cm)	Organic Carbon	137 _{Cs/} 40 _K	²¹⁰ Pb/ ⁴⁰ K
	0-5 510 10-15 15-20 20-30 30-40 40-50	2.7 2.4 3.2 1.5 2.2 2.0 1.9	0.39 0.12 0.08 0.02 <0.01 <0.01	0.26 0.14 0.16 0.12 0.11 0.12
2	0-5 5-10 10-15 15-20 20-30 30-42	4.5 2.4 4.8 4.3 4.3	0.47 0.35 0.48 0.56 0.48 0.34	0.28 0.16 0.26 0.32 0.22 0.13
3	0-5 5-10 10-15 15-20 20-30 30-35	4.1 2.4 2.5 2.5 2.4	0.60 0.58 0.59 0.56 0.61 0.81	0.50 0.53 0.44 0.52 0.48 0.53
4	0-5 5-10 10-15 15-20 20-30 30-35 40-52	1.9 1.0 1.0 0.6 1.3 1.1 2.3	0.03 0.02 <0.01 <0.01 <0.01 <0.01	0.12 0.10 0.12 0.07 0.11 0.11
5	0-5 5-10 10-15 15-20 20-30	2.3 3.5 2.3 2.0	0.39 0.37 0.41 0.72 0.26	0.16 0.17 0.17 0.19 0.17

Table 17. (continued)

Station Number	Depth (cm)	Organic Carbon	¹³⁷ Cs/ ⁴⁰ K	²¹⁰ Pb/ ⁴⁰ K
6		-		-
	0-5 5 - 10	2.1 1.7	0.42 0.36	0.47 0.37
	10-15 15-22	1.7 2.0	0.38 0.47	0.43 0.50
7				
	0-5 5-10	0.8 1.1	0.36 0.47	0.33 0.32
	10-15 15-20	1.2 1.2	0.57 0.31	0.25 0.29
7	20-30	2.0	0.10	0.22
7 (duplicate)	0-5	1.0	0.38	0.24
	5-10 10-15	1.9 2.5	0.54 0.62	0.29 0.31
	15-20 20-30	1.9 2.5 2.3 1.7	0.39 0.06	0.26 0.24
8	0-5 5-10	2.6 1.1	0.12 0.05	0.19 0.16
	10-15 15-20	1.2	0.04 0.06	0.15 0.13
	20-30	1.7	0.27	0.18
9	0-5	1.1	0.13	0.19
	5-10 10-15	1.0 1.3	0.13 0.10	0.16 0.16
	15-20 20-30	0.6 1.2	0.08 0.06	0.14 0.15
	30-40	2.7	0.07	0.19
10	0-5	1.3	0.11	0.25
	5-10 10-15	2.2 2.9	0.11 0.13 0.12	0.26 0.24
	15-20 20-30	1.5 1.1	0.04 0.06	0.22 0.18
	30-38	0.4	0.02	0.20

Table 18. Percent Sand, Silt and Clay in Sediment Cores as a Function of Depth (Sand < 62 $\mu m;$ Silt = 4-62 $\mu m;$ Clay < 4 $\mu m)$

Station Number	Depth	SAND	SILT	CLAY
1	0-10	21	39	40
	15-20	31	33	36
	40-50	11	49	40
2	0-10	46	49	5
	15-20	10	63	27
	30-42	49	10	41
3	0-10	12	63	25
	15-20	14	68	18
	30-35	16	70	14
4	0-10	79	14	7
	15-20	71	4	25
	30-40	8	40	52
5	0-10	17	42	41
	10-15	34	47	19
	20-30	25	61	14
6	0-10	38	48	14
	10-15	23	57	20
	15-22	21	73	6
7	0-10	16	55	29
	10-15	11	49	40
	20-30	29	43	28
7 (duplicate)	0-10 10-15 15-20	16 10 15	52 54 47	32 36 38
8	-10	8	58	34
	10-15	3	65	32
	20-30	38	42	20
9	0-10	56	27	17
	15-20	73	14	13
	30-40	55	31	14
10	0-10	10	63	27
	15-20	77	10	13
	30-38	71	9	20

Table 19. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 1

			Core	I (depth.	cm)		
Compounds	0-5	5-10	10-15	15-20	20-30	30-40	40-50
naphthalene	35	21	7	<4	6	<6	<5
2-methynaphthalene	49	16	8	8	8	<5	6
1-methynaphthalene	< 24	<4	<4	<4	<3	<5	<4
biphenyl	26	15	9	9	10	6	5
2.6-dimethylnaphthalene	7 7	4	11	10	<3	<5	< 4
2,3,5-trimethylnaphthalene	<20	10	16	5	<3	<5	<4
fluorene	72	17	18	12	<4	<6	< 5
dibenzothiophene	180	20	46	30	<19	<32	<27
phenanthrene	665	136	44	21	15	6	10
anthracene	324	80	19	23	<3	<5	< 4
1-methylphenanthrene	294	54	32	20	18	<5	9
fluoranthene	1,640	275	115	94	15	<5	< 5
pyrene	6,102	1,865	753	188	49	<5	< 5
benzanthracene	1,284	316	21	37	9	32	<8
chrysene	4,688	1,339	458	131	127	38	<8
benz(e)pyrene	7,098	2,804	986	251	235	<21	<17
benz(a)pyrene	5,467	1,934	1,015	488	548	245	134
perylene	547	499	347	<u> 267</u>	199	<u>202</u>	<u>190</u>
Total aromatics	28,546	9,405	3,905	1,594	1,239	529	354

Table 20. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 1

		Con	e 1 (depti	n, cm)		
0-5	5-10	10-15	15-20	20-30	30-40	40-50
19	20	10	9	6	5	<4
52	67	26	21	9	8	<5
<1	<1	<1	<1	< 1	<1	<1
<22	10	<3	< 3	< 4	<1	<8
<12	3	<2	< 2	< 2	<2	< 4
<2	<3	1	<2	< 2	<1	<1
9	2	<1	<1	<1	<1	<1
9	<1	<1	<1	<1	<1	<1
71	87	36	30	15	13	<10
_18	15	_ <u>1</u>	2	< <u>10</u>	<u><6</u>	<u><15</u>
89	102	37	32	15	13	25
	19 52 <1 <22 <12 <2 9 9 71 _18	19 20 52 67 <1 <1 <22 10 <12 3 <2 <3 9 2 9 <1 71 87 18 15	0-5 5-10 10-15 19 20 10 52 67 26 <1	0-5 5-10 10-15 15-20 19 20 10 9 52 67 26 21 <1	19 20 10 9 6 52 67 26 21 9 <1	0-5 5-10 10-15 15-20 20-30 30-40 19 20 10 9 6 5 52 67 26 21 9 8 <1

Table 21. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 2

	Core 2 (depth, cm)							
Compounds	0~5	5-10	10-15	15-20	20-30	30-42		
naphthalene	200	139	137	194	150	104		
2-methynaphthalene	125	33	43	64	55	49		
l-methynaphthalene	48	< 25	<16	<24	<31	<19		
biphenyl	.87	40	31	50	<26	45		
2,6-dimethylnaphthalene	<31	<24	<15	<23	<29	<18		
2,3,5-trimethylnaphthalene	<28	<22	<14	< 21	<26	<16		
fluorene	218	35	38	80	75	98		
dibenzothiophene	353	<150	<94	75	<184	294		
phenanthrene	1,039	366	406	639	542	522		
anthracene	367	240	260	365	358	357		
l-methylphenanthrene	378	299	184	167	189	2,431		
fluoranthene	1,409	1,884	1,275	1,614	1,621	5,087		
pyrene	2,772	1,498	1,388	1,885	1,950	2,949		
benzanthracene	1,385	775	832	1,650	1,130	3,012		
chrysene	4,202	2,482	2,682	5,381	3,546	6,697		
benz(e)pyrene	2,241	1,813	2,362	3,472	3,800	3,226		
benz(a)pyrene	1,149	949	1,172	1,698	1,543	1,664		
perylene	321	<u> </u>	282	530	488	42		
Total aromatics	16,294	10,720	11,092	17,864	15,447	26,96		

Table 22. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 2

		Core	2 (depth	cm)	
Compounds	0-5	5-10	10-15	15-20	20-30
Cl ₃ -butadiene-1	193	117	127	215	117
Cl ₃ -butadiene-2	851	286	352	1002	351
нсво	22	< 1	<1	<1	<1
Cl ₁ -biphenyl	10	20	16	64	33
Cl ₂ -biphenyl	40	<4	<3	14	15
Cl ₃ -biphenyl	56	6	7	39	35
Cl ₄ -biphenyl	45	2	4	76	26
Cl ₅ -biphenyl	52	3	4	59	11
Total chlorinated butadienes	1,066	403	479	1,317	468
Total chlorinated biphenyls	203	31	31	152	120
Total selected halogens	1,269	434	510	1,469	588

Table 23. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 3

		-	Core 3	(depth, cr	n)	
Compound	0-5	5-10	10-15	15-20	20-30	30-35
naphthalene	284	273	298	185	203	19
2-methynaphthalene	90	74	103	77	81	8
-methynaphthalene	38	< 22	55	<21	23	< 2
piphenyl	92	65	89	66	61	8
2,6-dimethylnaphthalene	< 32	<26	<19	<25	<23	< 2
2,3,5-trimethylnaphthalene	31	<20	<15	<19	<17	< 2
luorene	369	135	136	143	170	18
libenzothiophene	308	164	221	340	475	54
phenanthrene	1,719	948	823	922	1,124	1,18
anthracene	939	507	426	455	581	60
l-methylphenanthrene	598	388	212	220	107	23
fluoranthene	4,724	3,729	3,048	4,420	7,541	8,14
yrene	3,578	3,517	4,135	4,664	6,762	7,24
penzanthracene	1,687	1,749	1,886	2,388	5,707	6,94
chrysene	4,107	4,534	4,348	5,014	11,841	14,58
penz(e)pyrene	2,561	3,362	3,758	4,050	7,340	10,29
penz(a)pyrene	1,454	1,457	1,924	2,301	4,067	5,91
perylene	287	455	483	<u>586</u>	995	1,50
otal aromatics	22,866	21,357	21,945	25,831	47,078	57,75

Table 24. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 3

			Core 3 (de	epth, cm)		
Compound	0-5	5-10	10-15	15-20	20-30	30-35
Cl ₃ -butadiene-1	199	272	275	172	224	199
Cl ₃ -butadiene-2	571	800	749	452	567	492
HCBD	<1	<1	<1	3	5	7
Cl ₁ -biphenyl	32	55	70	60	217	145
Cl ₂ -biphenyl	40	26	27	199	433	475
Cl ₃ -biphenyl	39	31	17	42	97	78
Cl _A -biphenyl	34	28	66	75	199	125
C1 ₅ -biphenyl	51	78	166	184	892	1,633
Total chlorinated butadienes	770	1,072	1,024	627	796	698
Total chlorinated biphenyls	196	218	. 346	560	1,838	2,456
Total selected halogens	966	1,290	1,370	1,187	2,634	3,154

Table 25. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 4

			Core	4 (depth	1, cm)		
Compound	0-5	2-10	10-15	15-20	20-13	30-40	40-52
naphthalene	116	54	34	<3	<4	<4	<4
2-methynaphthalene	16	16	<3	27	29	30	37
1-methynaphthalene	15	10	<3	<3	5	<4	<4
biphenyl	21	14	5	<3	<3	8	9
2,6-dimethylnaphthalene	22	20	<3	4	4	<4	<4
2,3,5-trimethylnaphthalene	31	20	6	<3	< 4	<3	<4
fluorene	87	10	10	<3	<4	3	9
dibenzothiophene	91	36	38	10	57	41	100
phenanthrene	295	106	<3	<3	12	5	17
anthracene	93	46	16	20	33	25	33
1-methylphenanthrene	45	38	5	y	18	11	20
fluoranthene	775	289	14	<3	7	6	7
pyrene	451	274	30	<3	7	6	4
benzanthracene	234	36	7	49	11	109	101
chrysene	505	269	19	<5	99	54	72
benz(e)pyrene	8	444	16	<12	<16	<15	<16
benz(a)pyrene	147	179	47	86	104	85	226
perylene	40	321	_47	15	<u>17</u>	6_	<u>17</u>
Total aromatics	2,992	2,182	294	216	399	386	669

Table 26. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 4

			Co	re 4 (dep	th, cm)		
Compound	0-5	5-10	10-15	15-20	20-30	30-40	40-52
Cl ₃ -butadiene-1	64	7	4	7	8	5	11
Cl ₃ -butadiene-2	208	4	['] 7	< 4	< 4	3	7
HCBD	< 1	<1	< 1	< 1	< 1	<1	< 1
Cl ₁ -biphenyl	103	< 5	< 3	< 6	< 7	< 4	< 4
Cl ₂ -biphenyl	21	5	2	< 3	< 4	<2	< 2
Cl ₃ -biphenyl	8	4	< 1	< 1	< 1	1	1
Cl ₄ -biphenyl	9	2	<1	<1	< 1	< 1	4
Cl ₅ -biphenyl	13	< 1	<1	< 1	< 1	< 1	<1
Total chlorinated butadienes	272	11	11	7	8	8	18
Total chlorinated biphenyls	154	11	2	< 12	< 14	1	5
Total selected halogens	426	22	13	7	8	9	23

Table 27. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 5

		C	ore 5 (dept	h, cm)	
Compound	0-5	5-10 ¹	10-15 ¹	15-20 ¹	20-30
naphthalene	480	484	495	656	420
2-methynaphthalene	129	128	166	179	14
l-methynaphthalene	59	57	71	65	7
oiphenyl	93	180	244	103	9
2,6-dimethylnaphthalene	93	226	223	109	8
2,3,5-trimethylnaphthalene	54	240	382	49	4
fluorene	172	144	402	217	14
dibenzothiophene	197	216	578	598	17
phenanthrene	1,175	25,014	37,088	2,276	91
anthracene ·	307	396	510	542	43
l-methylphenanthrene	289	1,397	2,006	766	14
fluoranthene	1,490	5,831	9,857	2,197	1,49
pyrene	3,412	3,411	4,943	2,830	2,68
oenzanthracene	578	798	1,379	536	1,10
chrysene	1,328	1,701	2,940	2,919	2,26
penz(e)pyrene	2,069	2,264	1,667	3,038	2,87
penz(a)pyrene	1,683	1,932	1,655	2,211	2,29
perylene	185	<u> 164</u>	137	338	37
Total aromatics	13,793	44,583	64,743	19,629	15,76

¹Some of the concentrations reported in the region of fluorene to pyrene (i.e., phenanthrene) are high as a result of interference due to the high concentrations of chlorinated biphenyls present in these samples. Thus, concentrations of aromatics in these regions for these core sections must be viewed with caution.

Table 28. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 5

		Co	re 5 (depth,	cm)	
Compounds	0-5	5-10	10-15	15-20	20-30
Cl ₃ -butadiene-1	1,213	1,184	975	585	462
Cl ₃ -butadiene-2	2,731	2,871	2,686	1,536	1,688
HCBD	7	2	12	6	4
Cl ₁ -biphenyl	164	141	646	229	113
Cl ₂ -biphenyl	301	105	178	150	123
Cl ₃ -biphenyl	105	3,327	2,930	1,396	57
Cl ₄ -biphenyl	62	95	136	76	64
Cl _s -biphenyl	121	88	161	122	128
Total chlorinated butadienes	3,951	4,057	3,673	2,127	2,154
Total chlorinated biphenyls	753	3,754	4,051	1,973	383
Total selected halogens	4,704	7,811	7,724	4,100	2,537

Table 29. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 6

		Core 6	(depth, cm)
Compound	0-5	5-10	10-15	15-20
naphthalene	547	356	909	1,186
2-methynaphthalene	241	118	328	438
l-methynaphthalene	104	46	172	215
biphenyl	132	98	168	196
2,6-dimethylnaphthalene	103	105	187	233
2,3,5-trimethylnaphthalene	19	22	22	63
fluorene	482	278	658	1,055
dibenzothiophene	372	197	598	312
phenanthrene	2,014	1,182	2,755	4,359
anthracene	672	634	718	853
1-methylphenanthrene	1,028	127	187	329
fluoranthene	60	61	112	17:
pyrene	74	78	85	3,439
oenzanthracene	315	283	194	327
chrysene	954	952	1,245	1,764
benz(e)pyrene	690	1,037	28	514
benz(a)pyrene	251	747	902	786
perylene	<u>596</u>	34	142	189
Total aromatics	8,654	6,355	9,410	16,42

Table 30. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 6

		Core 6 (de	pth, cm)	
Compound	0-5	5-10	10-15	15-20
Cl ₃ -butadiene-1	8,057	18,445	35,010	23,280
Cl ₂ -butadiene-2	9,742	22,149	42,039	27,223
HCBD	19	106	49	46
Cl ₁ -biphenyl	177	5,189	3,593	548
Cl ₂ -biphenyl	549	1,590	1,466	415
Cl ₃ -biphenyl	71	214	237	412
Cl ₄ -biphenyl	166	96	129	110
C1 ₅ -biphenyl	95	183	218	83
Total chlorinated butadienes	17,818	40,700	77,098	50,551
Total chlorinated biphenyls	1,057	7,272	5,643	1,566
Total selected halogens	18,876	47,972	82,741	52,11

Table 31. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 7

		Cor	re 7 (depti	n, cm)	
Compound	0-5	5-10	10-15	15-20	20-30
naphthalene	361	173	147	271	265
2-methylnaphthalene	85	64	68	106	99
1-methylnaphthalene	58	3	45	72	73
biphenyl	54	34	33	44	54
2,6-dimethylnaphthalene	36	29	35	50	43
2,3,5-trimethylnaphthalene	39	35	39	71	56
fluorene	88	89	61	194	256
dibenzothiophene	136	93	127	295	436
phenanthrene	815	890	435	1,665	3,468
anthracene	151	138	122	368	482
1-methylphenanthrene	259	139	188	316	274
fluoranthene	1,553	1,215	727	2,089	4,339
pyrene	2,200	1,646	1,047	2,508	4,372
benzanthracene	17	125	286	1,597	1,963
chrysene	470	884	397	1,703	2,396
benz(e)pyrene	1,151	1,333	709	2,344	3,425
benz(a)pyrene	2,056	2,706	1,343	2,685	3,182
perylene	157	67	158	526	660
Total aromatics	9,686	9,661	5,967	16,904	25,853

Table 32. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 7 (duplicate)

	Core 7 (depth, cm)							
Compound	0-5	5-10	10-15	15-20	20-30			
naphthalene	350	208	140	408	35			
2-methylnaphthalene	92	85	79	146	14			
l-methylnaphthalene	63	56	52	17	10			
piphenyl	51	54	52	92	8			
2,6-dimethylnaphthalene	37	37	43	59	7			
2,3,5-trimethylnaphthalene	42	41	50	92	10			
fluorene	99	112	65	1,158	36			
dibenzothiophene	135	187	163	1,621	40			
ohenanthrene	736	942	374	16,688	2,88			
anthracene	176	283	141	1,950	49			
l-methylphenanthrene	168	184	161	719	34			
fluoranthene	1,014	1,643	522	20,874	3,23			
pyrene	1,553	1,957	854	18,555	3,50			
oenzanthracene	571	1,260	320	8,673	1,84			
chrysene	202	483	150	3,572	1,24			
penz(e)pyrene	1,062	1,900	658	13,942	2,91			
benz(a)pyrene	2,177	2,459	1,437	13,161	2,85			
perylene	225	434	202	3,061	75			
Total aromatics	8,753	12,325	5,463	104,889	21,70			

Table 33. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 7

		Cor	re 7 (depti	h, cm)	
Compound	0-5	5-10	10-15	15-20	20-30
Cl ₃ -butadiene-1	<3	11	14	19	9
Cl ₃ -butadiene-2	19	36	54	64	25
HCBD	<1	<1	<1	<1	<1
Cl ₁ -biphenyl	17	18	16	9	14
Cl ₂ -biphenyl	4	3	3	5	3
Cl ₃ -biphenyl	<1	6	1	1	<1
Cl ₄ -biphenyl	<1	1	13	9	2
Cl ₅ -biphenyl	3	7	9	<1	3
Total chlorinated butadienes	19	47	68	83	34
Total chlorinated biphenyls	24	35	42	19	22
Total selected halogens	43	82	110	102	56

Table 34. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 7 (duplicate)

	Core 7 (depth, cm)							
Compound	0-5	5-10	10-15	15-20	20-30			
Cl ₃ -butadiene-1	19	21	4	14	11			
Cl ₃ -butadiene-2	66	63	22	41	19			
HCBD	<1	<1	<1	<1	<1			
Cl ₁ -biphenyl	<21	39	26	39	11			
Cl ₂ -biphenyl	<12	3	3	4	3			
Cl ₃ -biphenyl	<2	1	1	3	<1			
Cl ₄ -biphenyl	<2	2	1	5	4			
Cl ₅ -biphenyl	<2	7	7	7	16			
Total chlorinated butadienes	85	84	26	55	30			
Total chlorinated biphenyls	<39	52	38	58	34			
Total selected halogens	85	136	64	113	64			

Table 35. Concentrations (µg/kg) of Selected Aromatic Hydrocarbons in Sediment Core 8

		Con	e 8 (dept	h, cm)	
Compound	0-5	5-10	10-15	15-20	20-30
naphthalene	2,434	34	13	37	813
2-methylnaphthalene	3,443	13	7	14	152
1-methylnaphthalene	631	16	11	17	23
biphenyl	573	20	17	18	104
2,6-dimethylnaphthalene	353	11	5	7	56
2,3,5-trimethylmaphthalene	19	20	5	21	70
fluorene	94	9	16	8	180
dibenzothiophene	86	<17	<17	<17	<17
phenanthrene	213	71	31	70	732
anthracene	82	30	12	27	360
1-methylphenanthrene	70	14	3	4	157
fluorantheme	36	110	27	170	408
pyrene	231	108	26	75	763
benzanthracene	333	101	34	75	1,474
chrysene	72	17	10	16	239
benz(e)pyrene	106	34	64	29	1,848
benz(a)pyrene	525	542	430	457	1,389
perylene	221	262	246	336	1,237
Total aromatics	9,522	1,412	957	1,381	10,009

Table 36. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons (naphthalenes and biphenyl) in Sediment Core Samples

Compound	All Cores, mean + SD ¹	Core 8 (0-5 cm)		
naphthalene	232 + 247 (n=53)	2,434		
2-methylnaphthalene	77 + 79 (n=58)	3,443		
1-methylnaphthalene	53 + 44 (n=38)	631		
biphenyl	55 + 51 (n=58)	573		
2,6-dimethylnaphthalene	55 + 62 (n=41)	353		

Except Core 8 (0-5 cm).

Table 37. Concentrations (µg/kg) of Selected Halogenated Organic Compounds in Sediment Core 8

	Core 8 (depth, cm)							
Compound	0-5	5-10	10-15	15-20	20-30			
Cl ₃ -butadiene-l	3	3	3	3	12			
Cl ₃ -butadiene-2	8	5	3	6	37			
HÇBD	1	1	1	1	1			
Cl _l -biphenyl	21	5	5	6	11			
Cl ₂ -biphenyl	3	3	20	3	3			
C1 ₃ -biphenyl	1	1 .	1	1	1			
Cl ₄ -biphenyl	1	1	1	1	1			
Cl ₅ -biphenyl	I	1	1	1	1			
Total chlorinated butadienes	8	8	7	6	49			
Total chlorinated biphenyls	21	11	20	6	11			
Total selected halogens	29	8	20	12	60			

Table 38. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 9

	Core 9 (depth, cm)							
Compound	0-5	5-10	10-15	15-20	20-30	30-40		
Naphthalene	154	113	58	47	41	50		
2-methylnaphthalene	66	45	25	19	28	22		
1-methylnaphthalene	61	52	28	20	26	22		
biphenyl	44	32	29	23	31	29		
2,6-dimethylnaphthalene	34	51	36	25	10	13		
2,3,5-trimethylnaphthalene	60	32	29	14	27	20		
fluorene	111	49	28	20	20	26		
dibenzothiophene	184	109	73	42	12	45		
phenanthrene	554	222	131	87	97	93		
anthracene	320	144	94	74	97	59		
1-methylphenanthrene	147	98	71	39	31	57		
fluoranthene	1,145	613	326	194	162	167		
pyrene	553	280	158	238	232	112		
benzanthracene	526	354	258	257	167	122		
chrysene	1,066	695	584	49	241	169		
benz(e)pyrene	402	310	248	107	140	108		
benz(a)pyrene	159	94	70	53	49	43		
perylene	278	185	<u>154</u>	72	69	75		
Total aromatics	5,864	3,478	2,400	1,830	1,480	1,232		

Table 39. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 9

	Core 9 (depth, cm)									
Compound	0-5	5-10	10-15	15-20	20-30	30-40				
Cl ₃ -butadiene-1	6	3	7	2	11	8				
Cl ₃ -butadiene-2	, 5	11	7	9	6	5				
1CBO	<1	<1	<1	1	1	<1				
Cl ₁ -biphenyl	8	11	<4	12	12	15				
Cl ₂ -biphenyl	27	<3	3	<2	<3	<2				
Cl ₃ -biphenyl	9	2	2	2	3	7				
Cl ₄ -biphenyl	67	2	55	36	12	8				
Cl ₅ -biphenyl	7	4	5	7	9	13				
Total chlorinated butadienes	11	14	14	11	17	13				
Total chlorinated biphenyls	118	19	65	57	36	43				
otal selected halogens	129	33	79	68	53	56				

Table 40. Concentrations ($\mu g/kg$) of Selected Aromatic Hydrocarbons in Sediment Core 10

	Core 10 (depth, cm)								
Compound	0-5	5-10	10-15	15-20	20-30	30-45			
Naphthalene	26	33	18	12	7	3			
2-methylnaphthalene	12	11	5	5	37	33 <3 2 3 <2 <2 8 2 22 13			
1-methylnaphthalene	21	4	<3	8	∹3	<3			
biphenyl	25	23	18	18	37	2			
2,6-dimethylnaphthalene	32	24	5	9	5	3			
2,3,5-trimethylnaphthalene	33	4	<3	4	<2	<2			
fluorene	19	39	5	23	5	<2			
dibenzothiophene	32	44	8	154	138	8			
phenanthrene	121	117	60	28	33	2			
anthracene	92	92	69	40	44	22			
l-methylphenanthrene	5 7	25	6	10	11	13			
fluoranthene	363	331	178	71	83	<3			
pyrene	228	285	124	106	149	6			
benzanthracene	174	210	142	13	21	6 <4			
chrysene	319	493	285	96	129	8			
benz(e)pyrene	23	225	133	22	<11	<10			
benz(a)pyrene	147	98	79	107	85	31			
perylene	<u>81</u>	118	58	20	_32	<u><7</u>			
Total aromatics	1,805	2,176	1,186	746	816	124			

Table 41. Concentrations ($\mu g/kg$) of Selected Halogenated Organic Compounds in Sediment Core 10

			Core 10	(depth, cm)	
Compound	0-5	5-10	10-15	15-20	20-30	30-38
Cl ₃ -butadiene-1	10	9	16	6	8	9
Cl ₃ -butadiene-2	<6	6	7	3	2	3
HCBD	<1	<1	<1	<1	<1	<1
Cl ₁ -biphenyl	11	21	9	<7	7	4
Cl ₂ -biphenyl	6	<3	5	<3	<2	<2
Cl ₃ -biphenyl	2	<1	<1	<1	<1	<1
Cl _A -biphenyl	1	1	<1	<1	<1	<1
CI ₅ -biphenyl	5	<1	<1	<1	3	<1
Total chlorinated butadienes	10	15	23	9	10	12
Total chlorinated biphenyls	25	22	15	<13	10	4
Total selected halogens	35	37	38	9	20	16

Table 42. Phenanthrene/Anthracene Ratios in Sediment Core Samples

	Depth (cm)							
	0-5	5-10	10-15	15-20	20-30	30-40	40-50	$\bar{x} \pm sp^1$
Core							 	
1	2.1	1.7	2.3	0.9	NC ²	NC	NC	1.8 ± 0.6
2	2.8	1.5	1.6	1.8	1.5	1.5		1.8 <u>+</u> 0.5
3	1.8	1.9	1.9	2.0	1.9	1.9		1.9 <u>+</u> 0.1
4	3.2	2.3	NC	NC	0.4	0.2	0.5	1.3 <u>+</u> 1.4
5	3.8	NC	NC	4.2	2.1			3.4 <u>+</u> 1.1
6	3.0	1.9	3.8	5.1				3.5 <u>+</u> 1.4
7	5.4	6.4	3.6	4.5	7.2			5.4 <u>+</u> 1.4
7 (duplicate)	4.2	3.3	2.7	8.6	5.8			4.9 <u>+</u> 2.4
8	2.6	2.4	2.6	2.6	2.0			2.4 <u>+</u> 0.3
9	1.7	1.5	1.4	1.2	1.0	1.6		1.4 <u>+</u> 0.3
10	1.3	1.3	0.9	0.7	0.8	NC		1.0 ± 0.3

 $[\]frac{1}{x} \pm SD$ (all samples) 2.5 \pm 1.7 (n=54).

²Not calculated because of the presences of interferences or because the compounds were below limits of detection.

Table 43. Concentrations of Selected Aromatic Hydrocarbons and Their Distributions Between Water, Suspended Matter and Surface Sediment

	Concentrations 1			Distributions (%)		
Compound	Water ²	Suspended Matter ³	Sediment ⁴	Water	Suspended Matter	Sediment
naphthalene	<0.003	700	480	<0.0003	59.3	40.7
2-methylnaphthalene	<0.003	196	129	<0.0009	60.3	39.7
1-methylnaphthalene	<0.003	138	59	<0.0015	70.1	29.9
fluorene	<0.004	236	172	<0.0010	57.8	42.2
phenanthrene	<0.004	1,109	1,175	<0.0002	48.5	51.5
anthracene	<0.004	326	307	<0.0006	51.4	48.4
1-methylphenanthrene	<0.004	1,010	289	<0.0003	77.8	22.2
fluoranthene	<0.004	1,912	1,490	<0.0002	56.2	43.8
pyrene	<0.004	2,789	3,412	<0.0001	45.0	55.0
benzanthracene	<0.004	899	578	<0.0003	60.7	39.3
chrysene	<0.004	1,763	1,328	<u><0.0001</u>	<u>57.0</u>	43.0
Total selected aromatics	<0.041	11,086	9,604	<0.0002	53.6	46.4

 $^{^{1}}$ Concentrations expressed in µg/1 for water and µg/kg dry wt $\,$ for suspended matter and surface $\,$

²sediment.
No data for aromatic hydrocarbons in water were collected as a part of this study. The values 3listed here were obtained from Riley et al. (1980, p. 51).
Numbers in this column were obtained by taking the mean hydrocarbon concentrations from Station 5 4during September, 1980, at 2 meters (see Table 7).
Data from Table 35.

Table 44. Concentrations of Selected Halogenated Organic Compounds and Their Distributions Between Water, Suspended Matter and Surface Sediment

		Concentratio	n ¹	Distribution (%)		
Compound	Water	Suspended Matter ²	Sediment ³	Water	Suspended Matter	Sediment
Cl ₃ -butadiene-1	252	616	1,213	12.1	29.6	58.3
Cl ₃ -butadiene-2	< 10	1,677	2,731	<0.2	38.0	62.0
HCBD	4	8	7	21.1	42.1	36.8
Cl ₁ -biphenyl	317	184	164	47.7	27.7	24.7
Cl ₂ -biphenyl	220	881	301	15.7	62.8	21.5
Cl ₃ -biphenyl	3	398	105	0.6	78.7	20.8
Cl ₄ -biphenyl	< 2	4,950	62	<0.1	98.8	1.2
Cl ₅ -biphenyl	< 2	893	121	<0.2	88.1	11.9
Total chlorinated butadienes	256	2,300	3,951	3.9	35.4	60.7
Total chlorinated biphenyls	540	4,298	753	9.7	76.9	13.5
Total selected halogens	796	6,598	4,704	6.6	54.5	38.9

 $^{^{1}}$ Concentrations expressed in $\mu g/1$ for water and $\mu g/kg$ dry wt for suspended matter and surface sediment. Numbers in this column were obtained by taking the mean hydrocarbon concentrations from Station 5

3during September, 1980, at 2 meters (see Table 13).

Data from Table 28.

Table 45. Input Rates (kg/yr) of Selected Individual and Classes of Organic Compounds to Hylebos and Blair Waterways

Component	Hylebos Waterway ¹	Blair Waterway ¹		
total aromatics	13.7	14.5		
benzanthracene	0.7	0.4		
benz(a)pyrene	0.6	0.2		
trichlorobutadienes	2.8	0.2		
hexachlorobutadiene	0.06	0.01		
chlorinated biphenyls	189	21		

Assumes surface areas of 4,670,000 and 6,430,000 sq ft for main channel areas of Hylebos and Blair Waterways and an average sedimentation rate of 0.7 cm/year. Concentrations for the selected organics were obtained from data in Tables 7 through 16.

Table 46. Concentrations ($\mu g/g$) of Isomeric Forms of Chlorinated Biphenyls from Core 5 (10-15 cm) as Determined by Battelle-Northwest and NOAA/NMFS

Isomeric Form of	Chlorinated Biphenyl Concentrations (% of Total)						
Chlorinated Biphenyls	Battelle-	NOAA/	NMFS				
Cl ₁ -biphenyl	6.7	1.2	2.0	1.3			
Cl ₂ -biphenyl	105.7	19.1	27.0	18.0			
Cl ₃ -biphenyl	203.3	36.8	49.0	32.7			
Cl ₄ -biphenyl	151.8	27.5	60.0	40.0			
Cl ₅ -biphenyl	80.9	14.6	12.0	8.0			
Cl ₆ -biphenyl	4.9	0.9	0.2	0.1			
Cl ₇ -biphenyl	ND^1		0.2				
Cl ₈ -biphenyl	ND		0.2				
Cl ₉ -biphenyl	ND		0.2				
Total chlorinated biphenyls	553		150				
$\frac{1}{ND}$ = not detected.							

ACKNOWLEDGMENTS

Special thanks to Donald W. Brown and the NOAA National Analytical Facility, Seattle, Washington, for their participation in the intercomparison study described in this report.

7. REFERENCES

Ambient Water Quality (1979): Criteria and Standards Division, Office of Water Planning Standards, U.S. Environmental Protection Agency, Washington D.C. Pollutant: Polynuclear aromatic hydrocarbons, Doc. #296 926; Polychlorinated biphenyls, Doc #296 803; Hexachlorobatadiene, Doc. #292 435.

Bean, R. M., D. C. Mann, and R. G. Riley (1980): Analysis of Organohalogen Products from Chlorination of Natural Waters Under Simulated Biofouling Control Conditions. NUREG/CR-1301, Nuclear Regulatory Commission, Division of Safeguards, Fuel Cycle and Environmental Research, Washington, D.C.

Bellar, T. A., and J. J. Lichtenberg (1974): Determining volatile organics at microgram-per-liter levels by gas chromatography. J. American Water Works Association 66:739-744.

Bennett, J. T. (1980): The biogeochemical significance of zooplankton fecal material in a biological productive, temperate Fjord. PhD. Thesis, University of Washington, Seattle.

Bopp, R. F., H. J. Simpson, C. R. Olsen, and N. Kostyk (1981): Polychlorinated biphenyls in sediments of the tidal Hudson River, New York. Environ. Sci. Technol. 15:210-216.

Bouever, E. J., B. E. Rittmann, and P. L. McCarty (1981): Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. <u>Environ. Sci. Technol.</u> 15:596-599.

Carpenter, J. H., and C. A. Smith (1978): Reactions in chlorinated seawater. In: Water Chlorination Environmental Impact and Health Effects, Vol. 2, Ann Arbor Science, Ann Arbor, Michigan.

Clark, R. C., Jr., and J. S. Finley (1973): Techniques for analysis of paraffin hydrocarbons and for interpretation of data to assess oil spill effects in aquatic organisms. In: Proc. 1973 Joint Conference on Prevention and Control of Oil Spills. API/EPA/USCG, March 13-15, Washington, D.C.

Giger, W., and C. Schaffner (1978): Determination of polycyclic aromatic hydrocarbons in the environment by glass capillary gas chromatography. <u>Anal.</u> Chem. 50:243-249.

Hardy, J. T. (1973): Phytoneuston ecology of a temperate marine lagoon. Limnol. Oceanogr. 18:525-533.

- Hardy, J. T., and M. Valett (1981): Natural and microcosm Phytoneuston communities of Sequium Bay, Washington. <u>Estuaries, Coastal Shelf Sci</u>. 12:3-12.
- Harvey, G. W., and L. A. Burzell (1972): A simple microlayer method for small samples. Limnol. Oceanogr. 17:156-157.
- Helz, G. R., and R. Y. Hsu (1978): Volatile chloro- and bromocarbons in coastal waters. Limnol. Oceanogr. 23:858-869.
- Hites, R. A., and K. Biemann (1972): Water pollution: organic compounds in the Charles River, Boston. Sci. 178:158-160.
- Hites, R. A., R. E. Laflamme, J. G. Windsor, Jr., J. W. Farrington and W. G. Deuser (1980): Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, U.S.A.). <u>Geochim. Cosmochim. Acta</u> 44:873-878.
- Jolley, R. L., H. Gorchev and D. H. Hamilton, Jr. (1978): Water Chlorination: Environmental Impact and Health Effects, Vol. 2, Ann Arbor Science, Ann Arbor, Michigan.
- Jolley, R. L., W. A. Brungs, and R. B. Cumming (1980): Water Chlorination. Environmental Impact and Health Effects, Vol. 3, Ann Arbor Science Publishers, Ann Arbor, Michigan.
- Lake J. L., C. Norwood, C. Dimock and R. Bowen (1979): Origins of polycyclic aromatic hydrocarbons in estuarine sediments. Geochim. Cosmochim. Acta 43:1847-1854.
- Lake, J. L., P. F. Rogerson and C. B. Norwood (1981): A polychlorinated dibenzofuran and related compounds in an Estuarine Ecosystem. <u>Environ. Sci.</u> Technol. 15:549-553.
- Malins, D. C., B. B. McCain, D. W. Brown, A. K. Sparks and H. O. Hodgins (1980): Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sounds. NOAA Technical Memorandum OMPA-2, National Oceanic and Atmospheric Administration, Boulder, Colorado.
- May, W. E., S. P. Wasik, and D. H. Freeman (1978): Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. Anal. Chem. 50:997-1000.
- McLafferty, F. W. (1967): Interpretation of Mass Spectra. W. A. Benjamin, Inc., New York, N. Y.
- National Academy of Sciences (1972): Particulate Polycyclic Organic Matter, 361 p. National Academy of Sciences, Washington, D. C.
- Nelson, C. R., and R. A. Hites (1980): Aromatic amines in and near the Buffalo River. Environ. Sci. Technol. 14:1147-1149.

- Olsen, C. R., H. J. Simpson, R. F. Bopp, S. C. Williams, T. H. Peng, and B. L. Deck (1978): A geochemical analysis of sediments and sedimentation in the Hudson Estuary. \underline{J} . Sed. Petrol. 48:401-418.
- Pavlou, S. P., and R. N. Dexter (1979): Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems. Testing the concept of equilibrium partitioning in the marine environment. Environ. Sci. Technol. 13:65-71.
- Prahl, F. G., and R. Carpenter (1979): The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochim. Cosmochim. Acta 43:1959-1972.
- Riley, R. G., E. A. Crecelius, D. C. Mann, K. H. Abel, B. L. Thomas and R. M. Bean (1980): Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49, U.S. Dept. of Commerce, Washington, D.C.
- Robbins, J. A., and D. N. Edgington (1975): Determination of recent sedimentation in Lake Michigan using lead-210 and cesium-137. <u>Geochim. Cosmochim. Acta.</u> 39:285-304.
- Schell, W. R., and A. Nevissi (1977): Heavy metals from waste disposal in central Puget Sound. Environ. Sci. Technol. 11:887-893.
- Sheldon, L. S., and R. A. Hites (1978): Organic compounds in the Delaware River. Environ. Sci. Technol. 12:1188-1194.
- Sheldon, L. S., and R. A. Hites (1979): Sources and movement of organic chemicals in the Delaware River. Environ. Sci. Technol. 13:574-579.
- Silker, W. B., R. W. Perkins, and H. G. Rieck (1971): A sampler for concentrating radionuclides from large volume samplers. Ocean Eng. 2:49.
- Spehar, R. L., G. D. Veith, D. L. DeFoe and B. V. Bergstedt (1979): Toxicity and bioaccumulation of hexachlorocyclopentadiene, hexachloronorbornadiene and heptachloronorbornene in larval and early juvenile fathead minnows, <u>Pimephales promelas</u>. Bull. Environ. Contam. Toxicol. 21:576-583.
- Strickland, J. D. H., and T. R. Parsons (1972): <u>A Practical Handbook of Sea-water Analysis</u>. Bulletin 167, Fish. Res. Board Canada, Ottawa.
- Windsor, J. G., and R. A. Hites (1979): Polycyclic aromatic hydrocarbons in Gulf of Maine sediments and Nova Scotia soils. <u>Geochim. Cosmochim. Acta</u> 43:27-33.

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APPENDIX A

SAMPLING METHODS

Sampling of Hylebos and Blair Waterways was conducted from a Battelle-Northwest research vessel anchored at each sampling site. Sediment cores were collected by divers. Sampling methods for water and suspended matter were similar to those used last year (Riley et al., 1980). The location of the stations for the collection of sediment cores, water, suspended matter, plankton, and surface microlayer samples in the waterways are shown in Figure 3.

Sampling of the waterways occurred in September and December 1980. Sediments were collected only in September 1980. In both September and December, water samples were collected on different days at three depths at two stations (surface, 2 m; midwater, 5 m; just above bottom, 9 m) and at a depth of 2 m at four additional locations in both waterways.

Samples consisted of: (1) suspended matter, water, plankton; (2) surface microlayer obtained at two locations and collected over an approximately 3-hr period; and (3) filtered water samples collected at four additional locations in each waterway. Plankton was collected from only the 2 m depths at two locations at which water was filtered for suspended matter. Samples of water were collected for "purge-and-trap" analysis below, adjacent to and above known discharge points at two locations in Hylebos Waterway and one location in Blair Waterway. Descriptions of sampling protocols for specific analyses are listed below.

Sampling for Total Suspended Solids, Chlorophyll, Particulate Organic Carbon, Dissolved Organic Carbon and Salinity

At each water column sampling station, samples were collected from three depths for total suspended solids, chlorophyll, particulate organic carbon, dissolved organic carbon and salinity. Suspended matter samples were collected in duplicate by pressure filtration of 1 to 3 l of seawater through a 0.4 μm membrane filter. Water was collected for filtration by pumping. After compressed air pressure filtration, the sample was rinsed with a small volume of high purity distilled water to remove soluble salts in order to determine an accurate weight of the suspended matter. The samples were refrigerated during transport and storage. Samples were collected for chlorophyll analysis by filtering a known volume of seawater through a 47 mm diameter membrane (0.4 μm) filter using the procedure described in Strickland and Parsons (1972). Particulate organic carbon samples were collected by filtration of several hundred ml of seawater through a precombusted glass fiber filter. The filter was stored frozen. Ten ml of the filtrate from each of the particulate organic carbon collections were stored under refrigeration prior to analysis for dissolved organic carbon.

Preparation of Samples for Dating Analyses

One hundred grams of sediment (oven dried at 70°C) were pressed into pellets 2 1/2" diameter). The pellets were gamma counted for the presence of ^{210}Pb , ^{137}Cs and ^{40}K .

Sampling of Water for Volatile Organic Compounds (Purge-and-Trap Method)

Glass bottles (125 ml) were cleaned with soap and water, rinsed rigorously with distilled water and dried in an oven at 120°C for several hours. The bottles were cooled and capped with a Hycar septum to prevent reintroduction of contamination prior to sample collection. Samples for "purge-and-trap" analysis were collected by removing the septum cap, completely filling the bottle with Puget Sound water and recapping with another Hycar septum. Three to four samples were collected at each sampling station. Samples were kept at wet ice temperature during the sampling cruises and during transport to the laboratory. At the laboratory, samples were stored in the refrigerator at 4°C until analyzed.

Sampling of Filtered Water for Halogenated Organic Compounds (XAD-2 resin method)

Preparation of Resin

XAD-2 resin was cleaned of impurities by three sequential Soxhlet extractions with methanol, acetonitrile and anhydrous ether, respectively. Each extraction lasted 24 hours. After the ether extraction, the resin was rinsed thoroughly with methanol and stored in a glass-stoppered jar under methanol.

Preparation of Resin Columns

Cleaned (sonicated in soap and water, rinsed with distilled water and dried with acetone) stainless steel columns (5/8" 0.D x 9" in length) fitted with Swagelok® stainless steel 5/8 to 1/4 inch reducing unions were connected to vacuum (aspirator). After addition of a plug of silanized glass wool to the bottom of the column, XAD-2 resin which had been slurried with methanol was added until sufficient space remained to add a small plug of glass wool at the top. Following addition of the resin, each end of the column was tightly sealed off with 1/4 inch stainless steel plugs. The columns were stored in a refrigerator until they were used.

Sampling at Station

During the collection of suspended particles, the glass filtered water was sampled by pumping 20 liters of water over XAD-2 resin contained in the small stainless steel columns. The columns were stored refrigerated until analyzed.

Sampling of Suspended Matter for Aromatic Hydrocarbon and Halogenated Organics Analysis

Suspended particulates were collected in duplicate at each depth by filtration of approximately 2,000 l of water through a glass-filtered filter with an effective pore size of 0.5 μm . The filters were precleaned by combustion at 450°C for two hours. The glass filters retained 98% \pm 0.5% of the particulate material compared to a 0.4 μm membrane filters. Sampling apparatus consisted of a steel pump, a PVC hose, and a PVC Battelle large volume filter holder (Silker et al., 1971). The filter holder held eight filters in parallel, each 30 cm in diameter. The sampling apparatus was precleaned with detergent. The system blank was insignificant due to filters, filter holder, pump, and hose. The particulate material was stored frozen in wide mouth glass jars containing metal-lined caps.

Sampling of Sediment for Aromatic Hydrocarbon and Halogenated Organics Analyses

Sediment cores, 30-50 cm long, were collected by SCUBA divers. Care was taken to avoid disturbing the sediment during collection and sectioning. Cores were sectioned into 5 or 10 cm sections and frozen in the field. Sampling sites were selected to complement those areas previously sampled by the National Marine Fisheries Service and with consideration for suspected pollution outfalls and post dredging activities. Duplicate cores were collected at one site to obtain some information regarding within-station variability.

Sampling of Water from Surface Microlayer for Aromatic Hydrocarbon and Halogenated Organics Analyses

Surface microlayer samples (1 l each) were collected by dipping a clean sheet of glass vertically in and out through the surface. The water layer remaining on the glass after each dip was scraped off with a metal scrapper and collected. The method which collects water from the upper 50-60 μm of the sea surface is a standard technique used for microlayer sampling (Harvey and Burzell, 1972). A subsample of each microlayer sample was preserved for microscopic examination.

Sampling of Phytoplankton

One phytoplankton sample was collected at each of two water column sampling stations (Fig. 3) by pumping a measured volume of water from 2 m depth first through a 243 μm net to remove most zooplankton and secondly through a 64 μm plankton net to retain phytoplankton. A split of each phytoplankton sample was preserved and later examined under a microscope to determine relative abundance of materials collected such as diatoms, microzooplankton, or wood fibers.

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			. Other controls
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APPENDIX B

ANALYTICAL METHODS

Total Suspended Matter

The concentration of total suspended matter ($\mu g/1$) was determined by weighing after drying at 60°C to constant weight.

Particulate Organic and Dissolved Organic Carbon

The concentrations of particulate organic carbon and dissolved organic carbon were determined by wet oxidation of carbon to $\rm CO_2$ in sealed ampoules after inorganic carbon was removed. The $\rm CO_2$ produced was quantified by IR light absorption using an Oceanography International carbon analyzer.

Chlorophyll a, Salinity and Temperature

The concentration of chlorophyll \underline{a} was determined by measuring the extinction of light in the acetone extraction solution, according to Strickland and Parsons (1972). Salinity was determined using a Hytech salinometer standardized with standard seawater. The temperature of the water exiting the pumps was determined with a laboratory thermometer.

Sediment Dating

The relative activities of ^{210}Pb , ^{137}Cs , and ^{40}K were determined in the dried, pressed sediment pellets prepared from sediment cores collected by divers and sectioned in the field. The ^{210}Pb activity was measured using an intrinsic gemanium diode (IGD) that is designed for counting low energy gamma rays (20-200 kev). The ^{210}Pb 47 kev gamma ray was counted by placing the sediment pellet on the IGD. The precision of the method for surface sediment is approximately $^+$ 10% for one standard deviation calculated on counting statistics.

The activities of ^{137}Cs , 662 kev and ^{40}K , 1460 kev gamma rays were measured simultaneously by counting the sediment pellets on a high resolution lithium drifted gemanium diode (geLi) equipped with an anticoincidence shield. The precision, based on counting statistics, was approximately $^+$ 3% for both ^{137}Cs and ^{40}K in the surface sediments.

Quantitative Analyses of Volatile Hydrocarbons in Puget Sound Waters (Purge-and-Trap Method)

The procedure used for this analysis is very similar to that discussed by Bellar and Lichtenberg (1974). A sample of water containing the volatile

organics is sparged with nitrogen gas and then passed through a stainless steel column packed with porous polymer beads (in this case, Tenax). Volatile organics, which are adsorbed on the polymer, are then introduced into the gas chromatograph (GC) or gas chromatograph/mass spectrometer (GC/MS) by heating the Tenax trap at about 200°C in a stream of helium. This process desorbs the organics from the trap and adsorbs them on to the front of the chromatographic column held at 0°C. After the volatiles have been introduced into the column, they are separated by conventional temperature-programmed gas chromatography.

An important part of the procedure is the prevention of water sample exposure to an air interface prior to sparging, since the volatiles are rapidly lost to air. To avoid this loss, two hypodermic needles were inserted through the sample bottle septum, one of which was attached to a 100 ml glass syringe fitted with a stopcock valve. About 80 ml of water sample was then carefully drawn into the syringe and the valve closed. Thirty-five milliliters of sample was expressed from the syringe into the sparging apparatus through a small-bore teflon tube, filling the apparatus from the bottom up. The remainder of the sample was stored in the syringe as a contingency sample. Just prior to sparging, 1 μl of an enthanolic solution of internal standard mixture containing 0.8 mg each of bromochloromethane, 1,4-dichlorobutane, and 1-chloro-2-bromopropane was added. Nitrogen purge of the sample was at 30 ml/min for 20 minutes.

Separation of volatile components was accomplished on a 2 mm ID glass 6-ft column packed with 0.2% carbowax 1500 on carbopack, using 20 ml/min helium carrier. After an initial hold at 0°C for sample introduction (5.5 min), the chromatographic oven was brought to 45° C in 1.5 min and then programmed at 8°C to 160° C. Instrumentation was a Hewlett-Packard Model 5985GC/MS System, including a Model 5840A Gas Chromatograph. Mass spectra were obtained by scanning in the electron impact mode from mass 45 to 320 at 180 amu/sec at an electron multiplier voltage of 2,200. Application of the method to the analysis of Puget Sound Waters has previously been reported (Riley et al. 1980).

Quantitative Analyses of Halogenated Organic Compounds in Water Following Adsorption on XAD-2 Resin

Hydrocarbons sorbed to XAD-2 resin were eluted with two 25 ml portions of ethyl ether. Following removal of the void volume of water, the remaining fraction of the first portion of ether was allowed to sit in the column for 15 min to allow exchange of sorbed components and then eluted from the column. This procedure was repeated with the second 25 ml portion of ether. Water underneath the combined ether extracts was removed with a Pasteur pipette and the ether was dried overnight in the presence of anhydrous sodium sulfate. The dried ether extracts were concentrated using Snyder columns, transferred to solu-vials and concentrated under a stream of nitrogen to 1 ml volumes. Following addition of 2-bromonaphthalene internal standard, the samples were analyzed on a Hewlett-Packard 5840 gas chromatograph equipped with a 50 m SP2100 quartz capillary column and electron capture detector. Chromatographic runs were programmed from 70 to 260°C at a rate of 4°/min following an initial

hold for 4 min. The run was held at 260°C for 15 min prior to recycle. Response factors for individual $\text{Cl}_1\text{-Cl}_5$ chlorinated biphenyls and hexachlorobutadiene on the electron capture detector were determined using authentic standards. Approximate response factors for the two trichlorobutadienes were determined by relating their concentrations as measured by FID relative to hexachlorobutadiene and their response in the electron capture detector.

Preparation of Suspended Particulate Matter Samples for the . Analysis of Aromatic Hydrocarbons and Halogenated Organics

Samples of suspended matter from Hylebos and Blair Waterways were Soxhlet extracted with benzene/methanol according to a published procedure (Clark and Finley, 1973). One half of each of the concentrated extracts was chromatographed over 15 g of silica gel. The columns were first eluted with 40 ml of hexane to remove nonpolar hydrocarbons and then eluted with 86 ml of hexane/methylene chloride 50/50 to elute a fraction containing aromatic hydrocarbons and the halogenated organic compounds. The fraction containing the aromatic hydrocarbons and halogenated organic compounds was concentrated under a stream of nitrogen to a volume of 1 ml. Following addition of a mixture of hexamethylbenzene and 2-bromonaphthalene internal standards, individual components in the extracts were separated, characterized, and quantitated by combinations of capillary gas chromatographic (GC) and capillary gas chromatographic/mass spectrometric (GC/MS) techniques.

Quantitation of Selected Aromatic Hydrocarbons and Halogenated Organic Compounds in Suspended Matter

Individual aromatic and halogenated organic compounds were separated and quantitated using a Hewlett-Packard 5840 gas chromatograph equipped with a 50 m SP-2100 quartz capillary column and flame ionization detector. The aromatic hydrocarbons that were quantitated were naphthalene, 2-methylnaphthalene, 1-methynaphthalene, biphenyl, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, fluorene, dibenzothiophene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benz(e)pyrene, benz(a)pyrene and perylene.

A standard mix of halogenated organic compounds consisting of hexachlorobutadiene, one each of the chlorinated benzene isomers and one each of the chlorinated biphenyl isomers (Cl_1 - Cl_5) was used to quantitate these classes of compounds in the suspended matter extracts.

Preparation of Sediment Samples for the Analyses of Aromatic Hydrocarbons and Halogenated Organic Compounds

Samples of sediment (100 g, wet wt) were placed in 150 ml Corex centrifuge tubes. Each sample was shaken twice with two 50 ml portions of methanol to remove the water. The methanol extracted sediments were slurried with methanol

and transferred to Soxhlet thimbles and Soxhlet extracted with benzene/methanol according to the procedure of Clark and Finley (1973). The Soxhlet extracts were combined with the two methanol extracts and rotary evaporated to near dryness. The concentrated extracts were transferred to 5 ml volumetric flasks. One ml (20%) of each was subjected to silica gel chromatography and GC and GC/MS analysis according to the procedures described for the organic chemical analysis of suspended matter.

Preliminary Screening of Suspended Matter and Sediments for Halogenated Organic Compounds

Samples of suspended matter and sediment from the waterways were screened for the presence of halogenated organic compounds using a Hewlett-Packard 5840 gas chromatograph equipped with a 50 m SP2100 quartz capillary column and electron capture detector. Individual compounds in samples showing significant electron-capturing activity were then quantitated by GC employing an electron capture detector.

Characterization of Aromatic Hydrocarbons and Halogenated Organic Compounds in Suspended Matter and Sediment by GC/MS

Chemical characterization of aromatic hydrocarbons and halogenated organic compounds associated with suspended matter and sediment was conducted using a Hewlett-Packard 5840-A gas chromatograph containing a 50 m SP2100 quartz capillary column operating in the splitless mode and coupled to a 5985 GC-equipped with 7900A and 7920 disc drives and operating in the electron impact and chemical ionization modes. Samples contained in heptane were injected into the gas chromatograph at $70\,^{\circ}$ C, held at that temperature for 4 min and programmed at $4\,^{\circ}$ /min to a final temperature of $260\,^{\circ}$ C. Assignments of structure were based on comparison to literature spectra. For organic compounds containing chloriné, the number of atoms of chlorine contained in a compound was established by comparison of chlorine isotope ratios of detected compounds to those reported by McLafferty (1967).